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GENERALIZATION OF WATER QUALITY CRITERIA USING CHEMICAL MODELS -- Development of the REDEQL-UMD System of Computer Programs for Aqueous Equilibria

Part I

REDEQL-UMD

A Users Manual for the Aqueous Chemical Equilibrium Modeling Program REDEQL-UMD

Donald K. Harriss, Sara E. Ingle, David K. Taylor, and Vincent R. Magnuson

Department of Chemistry
University of Minnesota-Duluth
Duluth, Minnesota 55812

Grant R804996

Project Officer

Gary E. Glass

Environmental Research Laboratory-Duluth
Duluth, Minnesota 55804

ENVIRONMENTAL RESEARCH LABORATORY-DULUTH
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
DULUTH, MINNESOTA 55804

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16. ABSTRACT

This research program had the primary objective of developing site-specific water quality criteria for metals through correlating aquatic toxicity with activities of metal species. The project was not intended to carry out experimental studies but to make use of existing literature reports of metal toxicity to generate the correlations.

Inherent in these studies was the need for knowledge of the number of metal species present, and the relative amounts of each. To meet these needs a set of computer programs for finding equilibrium concentrations of metal complexes REDEQL-UMD, was developed, along with a stability constant data base and associated reference-footnote data bases.

Literature values of stability constants were adjusted to 25° C by application of thermodynamic principles.

Once speciation and toxicity data were available, a combination of factor analysis and multiple regression analysis was used to develop correlations. A detailed example involving toxicity of copper to Daphnia magna is included.

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ABSTRACT

The applications and limitations of a chemical equilibrium computer program, REDEQL-UMD, are described in this Manual. REDEQL-UMD allows the computation of equilibrium distributions of species concentrations in aqueous systems. The basic equilibria which may be treated include complexation, precipitation, oxidation-reduction, and adsorption.

The standard version of REDEQL-UMD allows simultaneous consideration of reactions involving 20 metals and 30 ligands although the program can be readily modified to treat up to 50 metals or 99 ligands. Similarly, up to 20 redox reactions can be handled in the standard version but, if required, the number can be increased to 60. Limits and changes in limits for all controlling parameters are described in the Programmers Manual for REDEQL-UMD [2].

An accompanying data base includes relevant data on the metals and ligands, thermodynamic stability constants for complexes, mixed complexes, oxidation-reduction reactions, solids, and mixed solids.

REDEQL-UMD is written in FORTRAN although this Manual allows use of the program without need for reference to the actual FORTRAN source code.

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I. INTRODUCTION

I-A. Applications and Limitations of the Program

This guide describes the use of REDEQL-UMD, a computer program for predicting the distribution of chemical species at equilibrium in an aqueous system. This program is an outgrowth of the programs REDEQL2 and REDEQL.EPAK [1]. REDEQL-UMD provides a significant increase in chemical and computational capability over REDEQL2 and REDEQL.EPAK while also providing simplified input for the novice user and extensive diagnostic printouts to assist the user when problems are encountered. (Since the name REDEQL-UMD requires ten characters while the internal computer program name is restricted to seven, this program is occasionally referred to as UMDEQ in this and associated materials.)

REDEQL-UMD is useful in analytical and predictive work. For analytical field data the program can, for example: 1) predict speciation among free and complexed forms, and 2) compare ion products to solubility constants in order to determine which minerals are controlling aquatic equilibria. The former results, some of which cannot be measured, often are needed in toxicity studies. In modeling applications the program might: 1) predict the fate of a chemical introduced into a well-characterized body of water, 2) predict the results of mixing two bodies of water, 3) simulate or/and confirm laboratory experiments, 4) predict removal of chemicals through precipitation under varying conditions of pH, redox potential, and ionic strength, or 5) help in the design of buffered systems for biological studies.

The program has been written to provide great flexibility in equilibrium chemical modeling. The principal source of REDEQL-UMD's versatility is its generality. One way in which generality is maintained is by having a data base which is independent from the program source code. This independence enables the user to input any thermodynamic data desired for any combination of components. For many other programs, the source code must be revised to add even a single complex. With such programs it is easy for a user to forget the ramifications of changing one part of the program without changing some other portion. Another advantage of the REDEQL-UMD format is that the data file accompanying the program can be replaced with another data set. Thus, a user can reformat the data from another equilibrium program for use with REDEQL-UMD. In this manner one can compare program results for variations in calculation and in data.

The standard form of REDEQL-UMD requires $74K_8$ words of storage to compile on a CDC Cyber 171; however, the program has been written so that non-standard (smaller or larger) versions can easily be generated for special needs. While special data bases can be generated by the user, there is a program, TEMCORR, available for editing the large data base to select a smaller one appropriate to a given group of components. Use of a small data

base increases the speed of execution of REDEQL-UMD. This same program, TEMCORR, merges data from the thermodynamic file of constants at 25°C with a file of enthalpy values to create a data base for REDEQL-UMD at a temperature other than 25°C.

Emphases of this guide are explanation of input and interpretation of output. The source program is documented in the Programmers Manual for REDEQL-UMD [2]. The basic method of computation follows that published by Morel and Morgan in 1972 [3]. The format of the enthalpy data file distributed with this program and procedures for its combination with the formation constants to obtain thermodynamic constants for temperatures other than 25°C are described in Appendix G: Users Manual for TEMCORR. As described in Section VI, users may select, change, or update data in accordance with their needs.

Use of the program is illustrated with a straightforward example described in Section I-B. The information needed on each of the cards in the User Data Deck (input) is described explicitly in Section II. The use of various program options and the required data cards are described in Section III. Computer outputs from all examples are collected in Appendix B. The general contents of each output are described in Section IV. Error messages generated by the program are discussed in Section V. Section VI contains a description of the Thermodynamic Data Deck.

Chemical computer programs are not designed to replace chemists. They are tools available to chemists, engineers, ecologists, and others to assist in the solution of problems involving chemistry. Practice is required for the user to become skilled in use of the tool and chemical perception is required to know when its application is appropriate. These programs can be invaluable in the rapid solution of complex equilibrium problems, in data management, and in preventing the exclusion of often-overlooked chemical effects.

Each proposed application of the program should be considered carefully to see whether the desired results are within the capabilities of the program. The user must consider that:

1) The program predicts equilibrium distributions. The rates of dissolution, precipitation, complex formation, adsorption, and oxidation-reduction are not considered. Few natural systems are truly at equilibrium because of slow chemical processes, biological activity, and transport.

2) The data may be incomplete due to measurement of an insufficient number of parameters to completely specify the system, e.g. lack of measurement or characterization of organic matter, or incorrect assumptions as to which analytical determinations are critical to the study.

3) Formation constants reported in the literature may not have been accompanied by error limits or may have been measured in a medium, e.g., 4.0M potassium perchlorate, inappropriate to these studies.

4) Formation constants for important species may not yet have been measured or may have been missed in the literature search.

5) Ionic strength corrections are expected to be adequate only to 0.5M.

6) Solids in natural systems may not behave as pure phases due to surface modifications.

7) Very small concentrations reported in the output may be inaccurate due to computational limitations.

I-B. Demonstration of the Computer Program

A simple case involving 7 metals and 8 ligands will be presented to illustrate the utility of the program. For this sample calculation the pH and ionic strength are fixed. The metal and ligand concentrations are those found in Lake Superior for these metals and ligands.

The sample data and the appropriate input cards are shown in Figure 1. The contents of each card are described specifically in Section II. The type of card is given in the first two columns of each card. The types are named in Table 1 and fully explained in Table 2. This sample deck has six types of cards. Sample input coding sheets, which simplify preparation of the data deck, are shown in Appendix A. Outputs are explained in Section IV.

On the Deck Identification Card (0) a name is given to this data file. The Program Header Card (1) shows that 7 metals , 8 ligands, and 1 case will be considered. The Ionic Strength Card (2) gives the ionic strength, fixed for this case at 0.0012.

For each of 6 metals, its reference number (given in Table 3), a guess at the final concentration of the free ion, and its total concentration for each case are given on a Metal Card (3). Concentrations are expressed as -log M (molarity). The total concentration includes all dissolved and solid matter suspended in or in contact with one liter of solution. The seventh metal is H^+ which does not require a Metal Card (3).

The same information is given for each of 7 ligands on the Ligand Cards (4). The eighth ligand is OH^-. The pH card (5) contains the fixed pH.

I-C Interactive Version

The batch program REDEQL-UMD (UMDEQ) has been modified to allow for input of the User Data Deck in an interactive or time-sharing mode. Called EQLINTR, this version is described in Appendix F.

Metals	Ref.#	-logM
Ca^{2+}	1	3.5
Mg^{2+}	2	4.0
Na^{+}	5	4.3
Fe^{3+}	6	7.3
Zn^{2+}	12	6.8
Cr^{3+}	19	8.4

Ligands	Ref.#	-logM
CO_3^{2-}	1	3.1
SO_4^{2-}	2	4.5
Cl^{-}	3	4.4
I^{-}	6	8.1
SiO_3^{2-}	12	4.4
NO_3^{-}	57	4.7
CrO_4^{2-}	59	12.0

pH = 7.95
Ionic strength = 1.2×10^{-3}

Figure 1A. Sample data.

```
0  SHORT LAKE SUPERIOR DATA
1    7  8  1
2       1.2E-03
3  1   55     35
3  2   60     40
3  5   63     43
3  6   93     73
3 12   88     68
3 19  104     84
4  1   51     31
4  2   65     45
4  3   64     44
4  6  101     81
4 12   64     44
4 57   67     47
4 59  140    120
5      795
```

Figure 1B. Input cards.

Figure 1. Sample data and input cards.

II. THE USER DATA DECK

All of the card types used with the program are described in this section. A detailed explanation of each card is given in Table 2.

The cards always must be in numerical order by card type. If a card of the wrong type is read, the program will print on the output title page which type of card was read and which type of card it should have read. Execution of the program will stop at that point. Various other messages may be printed if the input is not in the right form or is not self-consistent. The user should carefully study the output of User Input Data to make sure that it agrees with what was supposed to be on the User Data Deck.

Data input sheets are shown in Appendix A. For floating point, F, formats the decimal point is positioned correctly on the input sheets so that numbers can be entered rapidly and decimal points need not be keypunched. Decimal points which are punched will override the implied decimal points. When exponential, E, formats are specified, a floating point format such as 0.002 will override the E format. When exponentials are used as signified with an E and/or $\pm$ in the field, the exponent should be moved to the far right of the field. Otherwise, 10^{-3} may become 10^{-30}, etc. When many fields are available for a list of the same type of things as in cards (9), (10), and (12), no fields should be left blank between fields that are used. The program will stop reading these data lines when it encounters a blank field and any information after that blank will be lost.

Table 1. User Data Deck Card Types

(0) Deck Identification Card
(1) Program Header Card
(2) Ionic Strength Card
(3) Metal Card
(4) Ligand Card
(5) pH Card
(6) CO_2 Card
(7) Redox Potential Card
(8) Electron Card
(9) Solids Card
(10) Redox Reactions Card
(11) N_2 Card
(12) Mixed Solids Card
(13) Adsorbing Surface Card
(14) Adsorbing Metal Card

Table 2. Program Input Cards: Card Sequence, Format, and Data Required.

Card Type	Field(s)	Card Column(s)	Description
(0)			Deck Identification Card: 1 card. Format I2,2X,19A4 Always required.
	1	2	0 (card identifier)
	2-20	5-80	Any desired free format message to identify deck and output.
(1)			Program Header Card: 1 card. Format I2,1X,20I3. All blanks are read as zeros. Always required.
	1	2	1 (card identifier).
	2	5-6	Number of metals including H^+($\leq$20).
	3	8-9	Number of ligands including OH^-($\leq$30).
	4	11-12	Number of cases ($\leq$10). See Section III-B.
	5	15	pH, fixed or calculated. 0 causes pH to be fixed. A value will be given for each case on card (5). 1 causes the program to calculate pH for each case. See Section III-E.
	6	18	Ionic strength, fixed or calculated. 0 causes the value of ionic strength given on card (2) to be used for all cases. 1 causes the program to compute ionic strength for each case.
	7	19-21	Charge adjustment. See Section III-D. 0 means no adjustment will be made for charge imbalance. N ,where 0<N<100, causes the total concentration of ion N to be varied to obtain a neutral solution. 100 causes the total concentrations of all ligands to be varied to obtain a neutral solution.

Table 2 (continued)

Card Type	Field	Card Columns	Description
	8	23-24	Charge on ion N, specified in field 7, at final pH of solution. Will differ from normal charge if the ion is hydrolyzed. Must be positive for a metal, negative for a ligand.
	9	27	Flag for inorganic carbon. See Section III-F. 0 means total inorganic carbon (if any) is given for ligand 1, card (4). 1 means carbonate alkalinity is given for total concentration of ligand 1, card (4). 2 means atmospheric CO_2 will control equilibria. Card (6) must be used. Large total inorganic carbon concentration also must be given.
	10	30	Redox Reactions. 0 causes oxidation-reduction to be ignored. 1 allows the redox reactions given to occur at a fixed redox potential. See Section III-G. 2 allows the redox reaction given to occur while the redox potential varies. See Section III-H.
	11	32-33	Solid phases to consider. -1 prevents all solids from precipitating. See Section III-I. 0 allows any solid to precipitate if the solution is supersaturated with respect to that solid. N ,where $0<N\leq 26$, is the sum of solids initially assumed to be present plus the solids which are not allowed to precipitate. See Sections III-I and III-J.
	12	36	Mixed solids to consider. 0 causes mixed solids not to be considered. 1 causes mixed solids to be considered. 2 causes mixed solids to be considered with some initially present or disallowed on card (12). 3 causes saturation ratios to be calcu-

Table 2 (continued)

Card Type	Field	Card Columns	Description
			lated for mixed solids but mixed solids are not allowed to precipitate. See Section III-K.
	13	39	Concentration Units. See Section III-L. 0 means input data are in units of -log M. 1 means input data are in units of mg/l.
	14	42	Adsorbing surfaces. See Section III-P. 0 means no adsorbing surfaces will be included. N ,where $0<N\leq 5$, is the number of adsorbing surfaces.
	15	45	Selects interaction intensity and/or capacity output routines. See Section III-N. 0 means no output. 1 causes interaction capacities to be printed. 2 causes interaction intensities to be printed. 3 causes both to be printed.
	16	48	Activity corrections. See Section III-O. 0 causes Magnuson equation to be used. 1 causes Davies equation to be used.
	17	51	Turns off printing of saturation ratios. 0 causes degree of saturation to be printed for all solids. 1 suppresses output containing saturation ratios.
	18	54	Selects units of concentration of complexes. 0 causes concentrations of complexes to be printed in moles/liter. 1 causes concentrations of complexes to be printed as activities and in moles/l.
	19	57	Turns off printout of concentrations of complexes. 0 causes concentrations of complexes to be printed. 1 suppresses output containing concentrations of

Table 2 (continued)

Card Type	Field	Card Columns	Description
			complexes.
	20	60	Turns off printing of thermodynamic data. 0 causes thermodynamic data printed both uncorrected as in the data base and as corrected to the final ionic strength for each case. 1 causes only the uncorrected thermodynamic data from the data base to be printed. 2 prevents all thermodynamic data from being printed.
(2)			Ionic Strength Card: 1 card. Format I2,3X,E9.3 Required only if field 6, Program Header Card, equals 0.
	1	2	2 (card identifier).
	2	6-14	Fixed ionic strength in moles/l.
(3)			Metal Cards: Number of metal cards is one less than the number of metals given in field 2 of the Program Header Card (no card for H^+). Format is 2(I2,1X),11(F5.3,1X) for -log (moles/l) or 2(I2,1X),(F5.3,1X), 10E6.2 for mg/l. Column numbers shown below in parentheses are for mg/l.
	1	2	3 (card identifier).
	2	4-5	Reference number of metal from Table 3.
	3	7-11	Guess of final free molar concentration for the first case. Must be -log (moles/l) regardless of units chosen for input of data. If zero is used for the guess, 10**(-8) is used by the program.
	4	13-17 (13-18)	Total concentration of metal for first case.

Table 2 (continued)

Card Type	Field	Card Columns	Description
			Must give a value greater than zero for first case, expressed as -log (moles/l). Must give value greater than 10^{-20} in mg/l. See Section III-L for proper choices of species mass.
	5	19-23 (19-24)	Total concentration for second case. If zero, value of previous case is used.
	6	25-29 (25-30)	Third case If zero, value of previous case is used.
	7	31-35 (31-36)	Fourth case.
	8	37-41 (37-42)	Fifth case.
	9	43-47 (43-48)	Sixth case.
	10	49-53 (49-54)	Seventh case.
	11	55-59 (55-60)	Eighth case.
	12	61-65 (61-66)	Ninth case.
	13	67-71 (67-72)	Tenth case.
(4)			Ligand Cards: Number of ligand cards is one less than the number of ligands given in field 3 of the Program Header Card (no card for OH^-) plus number of adsorbing surfaces in field 14. Sum must be ≤ 29. Format is 2($\overline{I}$2,1X),11(F5.3,1X) for -log (moles/l) or 2(I2,1X),(F5.3,1x), 10E6.2 for mg/l. Column numbers in parentheses are for mg/l. Adsorbing surface total concentrations

Table 2 (continued)

Card Type	Field	Card Columns	Description
			(numbers 90-95) also are given on these cards, always as -log (moles/l).
	1	2	4 (card identifier).
	2	5-6	Reference number of ligand from Table 3 or 90-95 for surface.
	3	7-11	Guess of final free molar concentration for the first case. Must be -log (moles/l) regardless of units chosen for input of remaining data. If zero is used for the guess, 10**(-8) is used by the program.
	4	13-17 (13-18)	Total concentration of ligand or surface for first case. Expressed as -log (moles/l) for surfaces, and -log (moles/l) or mg/l for ligands as discussed above. See Section III-L for proper choices of species mass.
	5-13	19-23 (19-24)	As for card type (3).
(5)			pH Card: 1 Card. Format I2,4X,10(F5.3,1X). Required if field 5 of Program Header Card is zero.
	1	2	5 (card identifier).
	2	7-11	Fixed pH of first case. If blank or 0, pH 8.0 assumed.
	3	13-17	pH of second case if fixed, assumed same as previous case if blank or zero.
	4	19-23	Third case. Assumed same as previous case if blank or zero.
	5	25-29	Fourth case.
	6	31-35	Fifth case.

Table 2 (continued)

Card Type	Field	Card Columns	Description
	7	37-41	Sixth case.
	8	43-47	Seventh case.
	9	49-53	Eighth case.
	10	55-59	Ninth case.
	11	61-65	Tenth case.
(6)			CO_2 Card: 1 Card. Format I2,4X,10(F5.3,1X). Used only if field 9, Program Header Card, is 2. See Section III-F.
	1	2	6 (card identifier).
	2	7-11	-log (CO_2 pressure in atm) for first case. 0 means equilibrium between CO_2(g) and CO_2(aq) is not considered.
	3	13-17	-log CO_2 pressure for second case. Blank or 0 causes value from last case to be used.
	4-11		Same fields, columns, and cases as card type (5).
(7)			Redox Potential Card: 1 Card. Format I2,2X,I1,1X,10(F5.3,1X). Used only if field 9 of the Program Header Card is 1 or 2. A guessed potential must be given for the first case, even when pE is to be calculated. For fixed potential, a value must be given for each case.
	1	2	7 (card identifier).
	2	5	Type of redox potential selected for input. See Section III-F. 0 means -log (electron activity).

Table 2 (continued)

Card Type	Field	Card Columns	Description
			1 means Eh in volts. 2 means dissolved O_2 in mg/l.
	3	7-11	Potential for first case (guessed or fixed). Blank or 0 means zero.
	4	13-17	Potential for second case if fixed. Blank or 0 means zero.
	5-12		Same columns and cases as for card type (5), fields 4-11.
(8)			Electron Card: 1 Card. Format I2,4X,10E6.2. Used only if field 9 of the Program Header Card is 2. An electron concentration must be given for each case.
	1	2	8 (card identifier).
	2	7-12	Electrons in redox solids and complexes included in the input for the first case (moles/l). May be negative. Blank or 0 means zero.
	3	13-18	Electron concentration for second case. Blank or 0 means zero.
	4	19-24	Electron concentration for third case.
	5	25-30	Fourth case.
	6	31-36	Fifth case.
	7	37-42	Sixth case.
	8	43-48	Seventh case
	9	49-54	Eighth case.
	10	55-60	Ninth case.
	11	61-66	Tenth case.

Table 2 (continued)

Card Type	Field	Card Columns	Description
(9)			Solids Card: 1 Card. Format 40I2. Used only if field 11 of Program Header Card is greater than zero. See Section III-I and III-J.
	1	1-2	9 (card identifier).
	2	3-4	Reference number of metal in first solid assumed present or not allowed.
	3	5-6	Reference number of ligand in first solid assumed present or not allowed.
	4	7-8	Position in the thermodynamic data base occupied by this solid among all solids this metal-ligand pair. If positive, solid is assumed present initially. If negative, solid is not allowed to precipitate.
	5	9-10	Metal in second solid.
	6	11-12	Ligand in second solid.
	7	13-14	Position of second solid in the thermodynamic data base, ± as above.
	8-10	15-20	Metal, ligand, and position of third solid.
	11-13	21-26	Fourth solid.
	14-16	27-32	Fifth solid.
	etc.		

If more than thirteen but fewer than twenty-six solids are to be imposed or disallowed, a second Type(9) card may be added, following the same format as above. The user must be sure that the first Type(9) card is completely filled, i.e. contains references to thirteen solids, as the program will cease acting on imposed-disallowed solids if blanks are found on the first card and the second card will then cause an abort.

(10) Redox Reactions Card:

Table 2 (continued)

Card Type	Field	Card Columns	Description
			1 card. Format 21(I2,1X). Used only if field 10 of the Program Header Card is greater than zero.
	1	1-2	10 (card identifier)
	2	4-5	Reference number of first redox reaction.
	3	7-8	Reference number of second redox reaction.
	4	10-11	Reference number of third redox reaction.
	etc.		
(11)			N_2 Card: 1 card. Format I2,4X,10(F5.3,1X). Used only if reaction 2 is specified on card (10). See Section III-O.
	1	2	11 (card identifier)
	2	7-11	-log (N_2 pressure in atm) for first case. Blank or 0 means equilibrium between $N_2(g)$ and $NO_3^-(aq)$ is not considered.
	3	13-17	-log (N_2 pressure in atm) for second case. Blank or 0 causes pressure of previous case to be used.
	4-11		Same fields, columns, and cases as for card type (5).
(12)			Mixed Solids Card: 1 card. Format I2,2X,19(1X,I3). Used only if field 12 of the Program Header Card is 2.
	1	1-2	12 (card identifier).
	2	6-8	Reference number of mixed solid.

Table 2 (continued)

Card Type	Field	Card Columns	Description
			If positive, solid is assumed to be initially present. If negative, solid is not allowed to precipitate.
	3	10-12	Reference number of second mixed solid, $\pm$ as above.
	etc.		
(13)			Adsorbing Surface Cards: Number of cards is equal to number of surfaces given in field 13 of the Program Header Card (≤ 5). Each card may be followed by several Metal Adsorption Cards (14). Format I2,3X,3F5.2,2I5,F5.2. See Section III-P.
	1	1-2	13 (card identifier)
	2	6-10	pH_{ZPC}
	3	11-15	$\log K^{s}_{a_2,intr}$
	4	16-20	$-\log K^{s}_{a_1,intr}$
	5	25	1 if field 4 is used. 0 if field 4 is not used.
	6	29-30	Number of metals which complex with this surface.
	7	33-35	Alpha (equals A in Manual)
	8	36-43	Name of surface
(14)			Adsorbing Metal Cards: Requires number given in field 6 of preceding Adsorbing Surface Card. Format I2,3X,I2,1X,I1,3(1X,F5.2,3(1X,I2))
	1	1-2	14 (card identifier).
	2	6-7	Reference number of metal.
	3	9	Number of metal-surface complexes (≤ 3).

Table 2 (continued)

Card Type	Field	Card Columns	Description
	4	11-15	log $*B^s_{intr}$ for the first complex. B used for beta in Manual.
	5	18	Stoichiometry of metal in the first complex.
	6	21	Stoichiometry of surface in first complex
	7	23-24	Stoichiometry of H^+ in the first complex.
	8	26-30	log $*B^s_{intr}$ for the second complex
	9	33	Stoichiometry of metal in the second complex.
	10		etc.

III. PROGRAM FEATURES

III-A Available Metals and Ligands

The metals and ligands for which the program and Thermodynamic Data File contain data are shown in Table 3, given on the following pages. Additional metals, ligands, and data may be added by the user; see Section VI.

Up to 19 metals plus hydrogen, and 29 ligands plus hydroxide may be considered at one time in the standard program. The total concentration of the metal or ligand in the solution plus that in solid and gas phases interacting with the solution must be known. An exception to this is total inorganic carbon which may be replaced by carbonate alkalinity or may be controlled by atmospheric CO_2. See Section III-F. The total concentration may be expressed as -log(moles/liter) or as milligrams/liter (see Section III-L). For the first case a finite value of -log M or mg/l must be given. All metals and ligands which are known to exist or which might be produced should be included, e.g., if one expects Fe(III) to be reduced to Fe(II), Fe(II) must be included in the list of metals at a finite concentration. If a metal or ligand is not to be considered in one or more cases of a multiple case run, a very low total concentration for it in that case (those cases) will prevent its significantly affecting other equilibria.

Table 3. Metals and Ligands for Which Data are Included
(Reference Numbers Shown Correspond to the REDEQL-UMD Data Base)

Metals

1. Ca^{2+}	12. Zn^{2+}	23. Be^{2+}	34. CH_3Hg^+
2. Mg^{2+}	13. Ni^{2+}	24. Sc^{3+}	35. Hg_2^{2+}
3. Sr^{2+}	14. Hg^{2+}	25. TiO^{2+}	36. Bi^{3+}
4. K^+	15. Pb^{2+}	26. Sn^{2+}	37. Sb^{3+}
5. Na^+	16. Co^{2+}	27. Sn^{4+}	38. Zr^{4+}
6. Fe^{3+}	17. Co^{3+}	28. La^{3+}	39. Tl^{3+}
7. Fe^{2+}	18. Ag^+	29. Ce^{3+}	40. In^{3+}

(continued)

Table 3 (continued)

Metals

8. Mn^{2+}	19. Cr^{3+}	30. Au^{+}	41. Rb^{+}
9. Cu^{2+}	20. Al^{3+}	31. Th^{4+}	42. Tl^{+}
10. Ba^{2+}	21. Cs^{+}	32. UO_2^{2+}	50. H^{+}
11. Cd^{2+}	22. Li^{+}	33. Cu^{+}	

Ligands

1. CO_3^{2-}	17. CIT^{3-}	33. ARG^{-}	49. SO_3^{2-}
2. SO_4^{2-}	18. OX^{2-}	34. ORN^{-}	50. SCN^{-}
3. Cl^{-}	19. SAL^{2-}	35. LYS^{-}	51. NH_2OH
4. F^{-}	20. $TART^{2-}$	36. HIS^{-}	52. MoO_4^{2-}
5. Br^{-}	21. EN^{0}	37. ASP^{-}	53. WO_4^{2-}
6. I^{-}	22. DIP^{0}	38. SER^{-}	54. AsO_4^{3-}
7. NH_3^{0}	23. $SUSAL^{3-}$	39. ALA^{-}	55. HVO_4^{2-}
8. S^{2-}	24. GLY^{-}	40. TYR^{2-}	56. SeO_3^{2-}
9. PO_4^{3-}	25. $GLUT^{2-}$	41. MET^{-}	57. NO_3^{-}
10. $P_2O_7^{4-}$	26. PIC^{-}	42. VAL^{-}	58. $DPTA^{4-}$
11. $P_3O_{10}^{5-}$	27. NTA^{3-}	43. THR^{-}	59. CrO_4^{2-}
12. $SiO_2(OH)_2^{2-}$	28. $EDTA^{4-}$	44. PHE^{-}	60. S_4^{2-}
13. $S_2O_3^{2-}$	29. $DCTA^{4-}$	45. ISO^{-}	61. S_5^{2-}
14. CN^{-}	30. $CYST^{2-}$	46. LEU^{-}	62. NO_2^{-}
15. AC^{-}	31. NOC^{3-}	47. PRO^{-}	63. AsO_3^{3-}
16. $ACAC^{-}$	32. $PHTH^{2-}$	48. $B(OH)_4^{-}$	64. $Au(OH)_4^{-}$
			99. OH^{-}

(continued)

Table 3 (continued)

Ligands

AC=acetate
ACAC=acetylacetate
CIT=citrate
OX=oxalate
SAL=salicylate
TART=tartrate
EN=ethylenediamine
DIP=dipyridyl
SUSAL=sulfosalicylate
GLY=glycine
GLUT=glutamate
PIC=picolinate
NTA=nitrilotriacetate
EDTA=ethylenediaminetetraacetate
DCTA=1,2-diaminocyclohexane-tetraacetate
CYST=cysteine
NOC=nocardamine (desferri-ferrioxamine)
PHTH=phthalate
ARG=arginine
ORN=ornithine
LYS=lysine
HIS=histidine
DPTA=diethylenetriaminepentaacetate
ASP=aspartate
SER=serine
ALA=alanine
TYR=tyrosine
MET=methionine
VAL=valine
THR=threonine
PHE=phenylalanine
ISO=isoleucine
LEU=leucine
PRO=proline

III-B Multiple Cases

Ten cases may be run at one time. Some parameters are constant for all ten cases and some may be varied. Iterations for the first case begin with free concentration equal to a guess provided by the user. This guess must be in units of -log (moles/l) whether the case data is in -log (moles/l) or (mg/l). If the user leaves the guess blank, the program will use 10**(-8) as the guess. For later cases the beginning free concentrations are the final free concentrations of the preceding case. For this reason, successive cases should not be too dissimilar, e.g., don't go from pH 9.5 to pH 4.0 in two successive cases.

Parameters which must be constant for all cases include:
- The metals and ligands considered.
- The ionic strength if fixed.
- The solids not allowed to precipitate.
- The redox reactions considered.
- The ion(s) used to adjust solution charge, if allowed.

The following parameters may be varied; if left blank, the value from the previous case will be used:
- Total concentrations of metals and ligands.
- pH, if fixed
- CO_2 or N_2 partial pressures if the gas phases are allowed.

The following must be given for <u>each</u> case:
- pE or other redox potential, if redox allowed.

Initial concentration of electrons, if required.

Examples of multiple cases are shown in Figures B7 and B15.

III-C Calculation of Ionic Strength

If field 6 of the Program Header Card is 1, the program will calculate the ionic strength of the solution after convergence is obtained. If ionic strength has changed by more than 0.5% from its last value, the program adjusts the thermodynamic data using activity coefficients appropriate to the new ionic strength and iterates until convergence is again obtained.

The final ionic strength calculated for each case is given in the Final Ion and Solid Concentrations output. When ionic strength is calculated, the thermodynamic constants corrected to that ionic strength normally will be printed for each case (see Section IV-B).

To include calculation of ionic strength for our sample case, field 6, column 18 of the Program Header Card is changed from a zero to a one. Output for this data is shown in Figure B2. Notice the additional iterations in Case Progress to achieve convergence at the calculated ionic strength.

III-D Charge Balance at Fixed pH

Charge balance need only be considered when pH is fixed. When pH is calculated, the total amount of hydrogen less total hydroxide is adjusted automatically to achieve charge balance. Balanced charge is required if the results of this computer run are to be used as input in runs where pH or pE will be calculated.

If fields 7 and 8 of the Program Header Card are blank or zero, total concentrations of metals and ligands will be constant. If the charge on the solution at convergence exceeds 0.1% of the ionic strength a warning message to that effect will be printed.

If field 7 is 100 and the charge on the solution exceeds 0.1% of the ionic strength at convergence, the program will adjust the total concentrations of all ligands proportionately and iterate until convergence is obtained and the charge on the solution is less than 0.1% of the ionic strength. The factor by which the concentrations have been adjusted is printed at the end of the Case Progress output and the total ligand concentrations as adjusted are given in the Final Ion and Solid Concentrations output. For the option of varying all ligand concentrations to achieve charge balance, field 7 of the Program Header Card is 100 as shown below:

```
1  7  8  1  0  1100
```

The Case Progress and Final Ion and Solid Concentration outputs for this

example are shown in Figure B3. In Case Progress, the number of iterations required is greatly increased.

If field 7 is a reference number, the total concentration of that ion will be adjusted. The usual charge of the ion, considering hydrolysis, at the fixed pH must be given in field 8. If the charge is negative it will be assumed to be a ligand. If adjustment of the total concentration of this ion would make it negative, the program defaults to adjusting all ligand concentrations. The Program Header Card for our sample case, adjusting chloride, is shown below.

1 7 8 1 0 1 3 -1

The consequent Case Progress and Final Ion and Solid Concentrations outputs are shown in Figure B4. The number of iterations required, as seen in Figure B4, is increased due to use of this option.

Because the charge is compared to ionic strength, ionic strength should always be calculated when the option to balance charge is used.

If the ion chosen to adjust charge balance is hydrolyzed at the designated pH, its charge will differ from the charge stored in the thermodynamic data, e.g., CO_3^{2-} carries a charge of -1 at pH 7.95 because it is primarily HCO_3^-. Therefore, if carbonate is the ion of choice to adjust charge belance at pH 7.95,-1 should be entered in field 7 on the Program Header Card. The ion chosen for adjustment should be one whose concentration is not well known, one which is predominant, or one whose concentration does not affect complexation (such as NO_3^-). The option to balance charge can greatly increase execution time especially when all ligands are adjusted. After studying output without charge balance, the user may wish to adjust total concentrations manually and then rerun the program rather than using one of the options outlined in this section.

III-E Calculation of pH

pH will be calculated for each case if a 1 is entered in field 5 of the Program Header Card. A pH card (5) is not needed if this option is used. The calculated pH, free hydrogen ion concentration, and total hydrogen less total hydroxide concentration are given in the Final Ion and Solid Concentration Output.

This option is recommended only for laboratory work where all components are known or for predictive work where two or more well characterized (including balanced charge) solutions are being mixed. This option should not be used with field data. The total concentrations of all metals, ligands, and electrons are used to calculate total hydrogen in the system by charge balance. If all metal and ligand total concentrations (including redox state) are not known exactly, the calculation of total hydrogen less total hydroxide concentration and the consequent pH will be meaningless.

Since the sample data are field data, the results of Section III-C when all ligands were adjusted are used to regenerate the pH. The computed pH should be 7.95. The sample data are shown in Figure 2. The Case Progress and Final Ion and Solid Concentrations outputs are shown in Figure B5.

```
0  SHORT LAKE SUPERIOR DATA WITH CALCULATED PH
1    7  8  1  1  1
3  1  55     35
3  2  60     40
3  5  63     43
3  6  93     73
3 12  88     68
3 19 104     84
4  1  5111   3111
4  2  6511   4511
4  3  6411   4411
4  6 10111   8111
4 12  6411   4411
4 57  6711   4711
4 59 14011  12011
```

Figure 2. Input data for calculated pH.

III-F Inorganic Carbon, Alkalinity, and CO_2 Partial Presure

The inorganic carbon in the system may be controlled in three ways: total inorganic carbon specified, carbonate alkalinity specified, or partial pressure of CO_2 specified. These three options are selected by placing 0, 1, or 2, respectively, in field 9 of the Program Header Card.

The default (field 9=0) requires entry of total inorganic carbon as -log (moles/l) or mg/l of CO_3^{2-}. The soluble carbonate alkalinity is printed in the Final Ion and Solid Concentrations output.

The alkalinity option (field 9=1) allows carbonate alkalinity as -log (meq/l) or 2 x mg CO_3^{2-}/l to be used. The total inorganic carbon calculated for this alkalinity and fixed pH is printed in the Final Ion and Solid Concentrations output. The concentration of free CO_3^{2-} is also given and the concentration of free HCO_3^- can be found in the Concentration of Complexes output. The alkalinity option can be used only when pH is fixed and only when carbonate containing solids are not present. The program does not correct for non-carbonate alkalinity except for free hydroxide and hydrogen.

A sample case with fixed carbonate alkalinity is shown in Figure B6. The alkalinity was assumed to be 7.87×10^{-4} meq/l. Note that the final total inorganic carbon is calculated to be 8.00×10^{-4} moles/l CO_3^{2-}.

The third option (field 9=2) is to allow pH and atmospheric CO_2 to

control the amount of inorganic carbon dissolved in the solution. The amount of carbonate in the aqueous system can be determined from pH and the partial pressure of CO_2 if one assumes the aqueous system to be at equilibrium with CO_2 in the atmosphere. Use of this option requires that values be given on the CO_2 Card (6). Zero in the first case means no equilibrium with CO_2 in the atmosphere will be considered; zero for any other case means same as the previous case. A typical partial pressure for CO_2 is $10^{-3.5}$ atmospheres. A CO_2 card for two or more cases (5 used) is shown below:

```
5     795   400   795   895
6      00  -3.5
```

On Card (4) for CO_3^{2-} (not shown), total CO_3^{2-} in the fifth case has been raised to 0.794M. The first case considers no CO_2; the next four have $10^{-3.5}$ atmospheres. The output for this example is shown in Figure B7. At low pH (4.00) in the second case the amount of CO_3^{2-} occurring as CO_2 is 7.9×10^{-4} moles/l while at pH 7.95 there are only 3.3×10^{-4} moles/l (Case 3), and at 8.95 (Case 4) CO_2 does not precipitate. Case Progress for Case 4 is shown so that the effects of dissolving CO_2 can be seen. In Case 5 the total concentration of CO_3^{2-} has been raised to 0.1M and 0.79 moles of CO_2 are formed per liter. Once the phase CO_2 precipitates, increasing the total amount of CO_3^{2-} has no effect on the amount of CO_3^{2-} in solution so long as the partial pressure of CO_2 is fixed. When this option is used, the total concentration of CO_3^{2-} includes CO_3^{2-} in the aqueous system and in the atmosphere and is meaningless.

When the atmospheric value of CO_2 is given for an equilibrium system, it sets, through the possible equilibria, the amount of CO_2 in every other possible form because of reactions such as those diagrammed below:

$$
\begin{array}{ccccccc}
CO_2 & \xleftarrow[K_s]{-H_2O} & H_2CO_3^{\circ} & \xleftarrow[K_1]{H^+} & HCO_3^- & \xleftarrow[K_2]{H^+} & CO_3^{2-} \\
 & & & & \Big| & & \Big| \\
 & & & & Na^+ & & Ca^{2+} \\
 & & & & \Big| K_{NaHCO_3} & & \Big| K_{CaCO_3} \\
 & & & & \downarrow & & \downarrow \\
 & & & & NaHCO_3^{\circ} & & CaCO_3^{\circ}
\end{array}
$$

(Many more complexes are formed than those shown above). Details of carbonate chemistry may be found in texts such as that of Stumm and Morgan [4].

The amount of each species will depend upon pCO_2, the constants, and free concentrations of H^+ and complexing metals. When pCO_2 is not given, the total CO_3^{2-} for the case is divided, according to the thermodynamic constants, among all possible forms excluding $CO_2(g)$. When pCO_2 is given, the total CO_3^{2-} given must be greater than the sum of all CO_3^{2-} species in equilibrium with that pCO_2. This means that excess CO_2 will escape from the system and be in the gas phase. The partial pressure of CO_2 is unaffected by "precipitation of CO_2" because the atmosphere is assumed large enough and

sufficiently mixed that CO_2 added to the atmosphere from the solution does not change the pCO_2.

If H_2CO_3 dissolves when the program begins iterations, it means that no CO_2 remains in the atmosphere because the system was not given sufficient total CO_3^{2-} to be in equilibrium with CO_2 at the given atmospheric pressure. The solution is undersaturated and "CO_2 dissolves" leaving no CO_2 in the atmosphere but not increasing total CO_3^{2-}. This obviously is not what one would expect to happen in a system in equilibrium with CO_2 in the atmosphere. To avoid this situation, total CO_3^{2-} should be increased until $CO_2(g)$ does not dissolve.

This option should be used only at fixed pH. If the solution is in contact with a sink/source of CO_2, the total hydrogen in the system will not be calculated correctly.

III-G Redox Reactions at Fixed Potential

If a 1 is present in field 10 of the Program Header Card, redox reactions are considered with the redox potential fixed for the calculation. The use of redox reactions at fixed potential requires cards (7) and (10); if the NO_3^-/N_2 redox reaction, 2, is included on Card (10), Card (11) also must be included.

The Redox Potential Card (7) contains a code for the type of potentials being used: 0 for pE, 1 for Eh in volts, and 2 for dissolved oxygen in mg/l. This code is followed by a specification of redox conditions for <u>each</u> case. Zero means zero for all cases. Dissolved O_2 can never be zero. Options 1 and 2 may be used <u>only</u> when pH is fixed and the redox potential is fixed. An example of Eh given for 5 cases is shown in Figure B9. Four different amounts of dissolved O_2 are used in Figure B10.

The Redox Reactions Card (10) identifies the redox reactions to be included, specified by reaction numbers as shown in Appendix C.

Card types (1), (7), and (10) are shown below for the consideration of two redox reactions, oxidation of Cr(III) (reaction 16) and formation of $Fe_3O_4(s)$ (reaction 13). The reactions are considered at five potentials, expressed as pE.

```
 1   7  8  5  0  0  0  0  0  1
 7   0 120    80    40    00   -40
10  16 14
```

Output for this example is shown in Figure B6.

A fixed redox potential should not be used with variable pH. Attempts to do so will result in warning messages. To calculate pH, the concentration and redox state of all metals and ligands must be known. If the redox states are known then redox consideration is unnecessary except to calculate pE (see

Section III-H).

To help the user select the redox equations which will be important under given circumstances, pE-pH plots of relative concentrations of primary species for the available redox equations are shown in Appendix D. The plots illustrate which redox reaction should be considered in which pE-pH regions. The curves are logs of activities or logs of ratios of activities of species. It should be necessary to consider a redox reaction only in the areas between logs equal to 10 or -10. Outside of these areas one species (or a solid) dominates and the other may be ignored for most purposes. Computational problems during program execution may occur if the redox reaction is considered in a region far outside the shaded areas.

For a redox equation involving two soluble species, the curves shown are for fixed values of the log of the ratios of product and reactant concentrations. For instance Figure D1, reaction 1, shows curves for log $[(Fe^{2+})/(Fe^{3+})]$ equal to 10, 5, and 0 (equal amounts of each). In the region where pE is less than 3 the prevalence of Fe^{2+} is so dominant that all iron could be considered Fe^{2+} and redox reaction 1 and Fe^{3+} could be ignored. When reactions involve one mole of product and one mole of reactant the curves do not depend on total concentrations. However, when product and reactant have unequal stoichiometry, curves also depend on total concentration. An example of this is shown by reaction 4, Figure D4. The total concentrations shown are the sums of the activities of free mercury (I) and free mercury (II). They do not necessarily represent total dissolved mercury. In this figure, the line labeled 15b represents the pE and pH conditions at which log $[(Hg^{2+})/(Hg_2^{2+})] = 15$ and $(Hg^{2+}) + 2(Hg_2^{2+}) = 10^{-5}$ M.

The presentations for solids differ slightly. As solubility decreases the concentrations of reacting species become necessarily smaller. The curves show under which pE and pH conditions a particular activity (usually 10^{-10}, 10^{-5}, and 10^{-1}M) would be in equilibrium with solid.

In regions where the maximum free concentration (free concentration in equilibrium with solid) of the reacting species is very small, that species can be considered to be in the solid form. For example, in reaction 22, Figure D22, at pH 8 and pE 12 most Mn^{2+} would be oxidized to $MnO_2(s)$.

Calculations involving redox reactions may produce fatal errors during computation. To avoid these, judicious selections of redox reactions must be made. Only two or three redox reactions should be added to the calculation at one time and pE and pH should not vary greatly between cases. If the pH and pE of the computation are such that the concentration of an ion in a redox reaction is less than 10^{-10}M or a ratio of concentrations of species linked by redox is less than 10^{-5} or greater than 10^{5}, the dominant form of the species should be used in the calculation and that particular redox reaction should not be considered.

It is well to remember that one is dealing with multiple simultaneous reactions. Precipitation of solids and formation of complexes may lead to large total concentrations of a species in a given oxidation state even

though the free concentration of that oxidation state is smaller than that of another oxidation state of the same element.

Caution must be exercised in use of the redox reactions because the kinetics of some are very slow, particularly the nitrogen reactions and those involving oxidation of solids. Some redox reactions might not be included because of their slow rates of reaction, if one is interested in short-term effects, or because biological activity maintains concentrations which are not at chemical equilibrium. As an example, NH_3 and NO_3^- often occur simultaneously in aquatic systems while their coexistence would not be predicted by the program. Whether this is caused by slow interchange (redox) or constant supply of one of them doesn't really matter. The user would want to leave both in the system and not use a redox equation.

III-H Redox Reactions with Change in Redox Potential

If a 2 is present in field 10 of the Program Header Card, the redox potential will be calculated when all components have reached redox equilibrium. This option requires cards (7), (8), and (10).

The Redox Potential Card (7) states the pE guess for the first case.

The Electron Card (8) specifies the "concentration" of electrons in the mixture. This will be zero if there are not any redox solids or complexes in the initial mixture; otherwise, it is the product of the redox solid or complex concentration and the stoichiometry of electrons in the redox reaction. It may be negative. This quantity is used for conservation of electrons and charge balance. The amounts of metals and ligands in these solids must be included in metal and ligand total concentrations, as always. "Free" electrons do not exist in solution so they cannot contribute to electron "concentration". As an example, we can use the output developed in III-G and calculate the electron concentration from Figure B6d. The only redox solid present is 1.67×10^{-8} M Fe_3O_4 which consumes one electron, so the electron concentration is 1.67×10^{-8} M.

The Redox Reactions Card (10) specifies the redox reactions to be included, given by reaction number as shown in Appendix C. Any redox solid formation reaction specified will cause that solid to be taken as initially assumed present, i.e. imposed.

Sample cards for redox with variable potential are shown in Figure 3 and the consequent output is in Figure B11.

This option should be used only with variable pH since many redox reactions change both pE and pH. Attempts to use this option with fixed pH will result in a warning message. All warnings which applied to use of variable pH (Section III-E) apply to variable pE and, in addition, the user must know the initial redox state of all species: which redox state(s) the metals and ligands are in, which redox solids and complexes are present initially and in what concentrations. This option will be useless if these

data are not available. The probable application of this option will be in predictive work on a mixture of two previously modeled systems for which sufficient information would be available.

```
 0  SHORT LAKE SUPERIOR DATA WITH REDOX WITH CAP.  AND INT.
 1   7  8  1  1  1  0  0  0  2  0  0  0  0  3
 3  1  55     35
 3  2  60     40
 3  5  63     43
 3  6  93     73
 3 12  88     68
 3 19 16802 14802
 4  1  5111  3111
 4  2  6511  4511
 4  3  6411  4411
 4  6 10111  8111
 4 12  6411  4411
 4 57  6711  4711
 4 59 10411  8411
 7     100
 8     167-08
10 16 13
```

Figure 3. Input data for variable pE.

III-I Solids Not Allowed to Precipitate

All solids may be disallowed (never allowed to precipitate) by placing a -1 in field 11 of the Program Header Card. This option for the sample case is shown below:

```
 1   7  8  1  0  0  0  0  0  0 -1
```

Saturation of Solids and Final Ion and Solid Concentrations output listings are shown in Figure B12.

Specific solids may be disallowed by placing the total number of solids disallowed plus those assumed to be present initially (see Section III-J) in field 11 of the Program Header Card. Up to twenty-six, disallowed plus assumed, may be considered. The specific solids to be disallowed are shown on the Solids Card (9). They are identified by the metal number, the ligand number, and the negative of the solid position among all solids of this metal-ligand pair. More than one solid per metal-ligand pair may be specified.

An illustration of disallowing one solid is described in Section III-J and shown in Figure B13.

III-J Solids Specified as Initially Present

Solids which are known to be in contact with the solution or which are expected to precipitate can be specified as initially present so that the solution will appear to be saturated with respect to the solid when the calculation is begun. This is not necessary but does increase the efficiency of the program especially when major ions are involved. Tthe sum of solids present and solids disallowed is entered in field 11 of the Program Header Card. The solids present are specified on the Solids Card (9). Each solid requires three fields. The first is the metal number, the second the ligand number, and the third (positive) is the solid position among all solids of this metal-ligand pair. More than one solid per metal-ligand pair may be specified.

The cards shown below would be used to disallow $ZnSiO_3$ and to require that $Fe(OH)_3$ and $CaSO_4$ are present initially.

```
1   7  8  1  0  0  0  0  0  0  3
91212-1 699 1 1 2 1
```

The output for this case is shown in Figure B13. Notice that $CaSO_4$ dissolves in Case Progress. Solids assumed present initially are only guesses; they will "dissolve" if the solution is not saturated.

III-K Mixed Solids

Mixed solids include more than one metal and/or more than one ligand. Those for which data are included in the Thermodynamic Data Deck are shown in Appendix E. Each is numbered. There are two types: 0, for two metals and/or two ligands, and 1 for alumino-silicate clays. If field 12 of the Program Header Card is 1, all mixed solids in the thermodynamic data deck will be included in the computations if their components are present. If field 12 of the Program Header Card is 2, some mixed solids may be assumed present initially or not allowed to precipitate, in which case a Mixed Solids Card (12) is required. The mixed solids present initially or not allowed to precipitate are specified by including their identifying numbers from Appendix D and making them negative if disallowed. If field 12 contains a 3, mixed solids will have their saturation checked but none will be allowed to precipitate. (Same as -1 for solids in field 11).

Mixed solid data will appear with the Thermodynamic Constants, the solids present, and the Distribution of Species output.

The Program Header Card for a case where all mixed solids are considered is shown below.

```
1   7  8  1  0  0  0  0  0  0  0  1
```

The output for this case is shown in Figure B14.

The Program Header Card and Mixed Solid Card for not allowing dolomite

(mixed solid 5) are shown below:

```
 1   7  8  1  0  0  0  0  0  0  0  2
12    -5
```

Results are shown in Figure B15.

III-L Milligram per Liter Input

Input data may be in mg/l if a 1 (one) is placed in field 13 of the Program Header Card. The guess for free concentration of the ion for the first case must however still be in units of -log (moles/l). This option has been introduced because field data are often available in these concentration units. Before preparing input data for use under this option, check the listing of metal and ligand species in the data base to ascertain which species are treated in terms of the principal atom rather than the entire ion, e.g., mg/l of nitrogen rather mg/l of nitrate (NO_3^-). Input data in this form produce the normal output routines in moles/l with the exception that the User Input Data will list concentrations both as mg/l and moles/l. Examples of input cards are shown in Figure 4 and output is shown in Figure B16.

```
0  SHORT LAKE SUPERIOR DATA WITH MG/L INPUT
1   7  8  1  0  0  0  0  0  0  0  0  1
2      1.2E-03
3  1  55   126+01
3  2  60   244+01
3  5  63   115+00
3  6  93    .0028
3 12  88    .0104
3 19 104   207-04
4  1  51     47.7
4  2  65     3.04
4  3  64     1.41
4  6 101   .00101
4 12  64     3.75
4 57  67     1.24
4 59 140   116.07
5     795
```

Figure 4. Input data in mg/l.

III-M Activity Coefficients

Activity corrections for ionic strength throughout the program normally are made using activity coefficients calculated according to the Magnuson equation from Sun, Harriss, and Magnuson [5]:

$$-\log \gamma = 0.509Z^2\{[\sqrt{I}/(1+1.51\sqrt{I})] - 0.08I\} - 0.09I$$

where Z is the charge of the species and I is the ionic strength. This equation was obtained from a statistical fit of stability constant data over a range of ionic strength from 0 to 0.5.

An alternative correction is the Davies equation [6]:

$$-\log \gamma = 0.509Z^2\{[\sqrt{I}/(1+\sqrt{I})] - 0.3I\}$$

This equation is considered useful to I = 0.1. At lower ionic strengths the two expressions become indistinguishable. The Davies expression can be used in place of the Magnuson expression by placing a 1 in field 16 of the Program Header Card. The activity expressions used to correct constants for ionic strength are identified at the top of the listing of Thermodynamic Data for Verification. The Program Header Card for using the Davies equation is shown below.

1 7 8 1 0 0 0 0 0 0 0 0 0 0 0 1

No output is shown for this option as the results are indistinguishable from those obtained using the Magnuson equation at the ionic strength of this example.

III-N Interaction Capacities and Intensities

Interaction capacities and intensities are a measure of the sensitivity of free concentrations to changes in total concentration. The output which prints interaction capacities is called by a 1 in field 15 of the Program Header Card. A 2 causes interaction intensities to be printed, and a 3 will cause both to be printed.

A capacity is defined as

$$\delta'_{XY} = -[\partial \log X/\partial TOTY] = \partial pX/\partial TOTY$$

where X is the free concentration of species X and TOTY is the total concentration of species Y. Capacities are symmetric, i.e. $\delta'_{XY} = \delta'_{YX}$, and they are defined for all species.

In Figure B11 are shown the interaction capacities for the example of a calculated redox potential (Section III-H). Large absolute values reflect a strong dependence of the free concentration on the total concentration. Each row represents one free concentration and its dependence on each total concentration. A column indicates which free concentrations will be affected by a change in one total concentration. In this example, a change in total iodide will affect only free iodide. A change in total iron will affect free concentrations of H^+, Ca^{2+}, Mg^{2+}, Na^+, Fe^{3+}, Zn^{2+}, Cr^{3+}, CO_3^{2-}, SO_4^{2-}, SiO_3^{2-} and e-; similarly, the free concentration of iron depends upon the total concentrations of each of these species. The logarithmic amount by which a free concentration will change with an increase in total Y of TOTY is estimated by

$$\Delta pX = (\delta'_{XY})(\Delta TOTY)$$

Careful examination of the matrix and use of this relationship may allow the user to adjust the free concentration of species X by increasing the total amount of Y. Y might be chosen so that it does not affect other parameters (free concentrations) which the user desires to maintain constant.

Interaction intensities are dimensionless. They are defined as

$$\delta_{XY} = (\partial \log X)/(\partial \log TOTY) = \partial pX/\partial pTOTY = TOTY\,\delta'_{XY}$$

They are not symmetric and are not defined for hydrogen or electrons because those species may have negative total concentrations; therefore, there are no values in the output corresponding to interaction intensities of hydrogen or electrons. Positive values of intensities indicate an increase in free concentration with increase in total concentration. Intensities show the relative change in the free concentration of one species, X, with the relative change in total concentration of another, Y, while capacities show the relative change in free concentration of one species, X, for a unit change in total concentration of another, Y. The intensities presented in Figure B13a show that, while free iron depended on many total concentrations according to the capacities, free iron will be affected most strongly by variations in H^+, Fe^{3+}, SiO_3^{2-} and e-. On the other hand, a relative change in total iron most strongly will affect the free concentrations of Fe^{3+}, Cr^{3+}, CrO_4^{2-}, and e-.

More detailed descriptions [7] of the application of interaction capacities and intensities may help the user to view the capacities and intensities as slopes of titration curves.

III-O Nitrogen Partial Pressures

Just as aqueous CO_3^{2-} can be controlled by atmospheric CO_2 and pH (see Section III-F), aqueous NO_3^- can be controlled by atmospheric N_2, pH, and pE. At fixed pE and pH, one can allow atmospheric nitrogen to be in equilibrium with NO_3^- in the system. This is accomplished by specifying redox reaction 2 on the Redox Reactions Card (10) and putting non-zero values for -log (partial pressure of N_2) on the Nitrogen Card (11). Atmospheric N_2 is usually 0.8 atm, the negative log of which is -0.1.

The cards for a redox case including a nitrogen atmosphere are shown below.

```
 1   7  8  5  0  0  0  1
 7   0 120    80    40    00    -40
10   2 16 13
11      1
```

Output for this case (like Section III-G) is shown in Figure B18. At high pH and high pE there may be insufficient NO_3^- to be in equilibrium with the

atmosphere. N_2 gas (called $(NO_3)_2H_{12}(s)$) will then dissolve. This is illustrated in the first case shown (Figure B18C).

III-P Adsorption

The adsorption routine contained in REDEQL-UMD is a surface complexation adsorption model adapted from that in REDEQL.EPAK. The prototype of this model was described in a draft of California Institute of Technology Technical Report EQ-76-01 by McDuff and Morgan [8]. Their work was patterned after that of Schindler et al. [9], Hohl and Stumm [10], and Vuceta [11]. Only "ligand" surfaces are considered. There are no thermodynamic data on file; data must be provided by the user. The constants given here are for the purpose of example only. Experimentally determined adsorption constants depend heavily upon the hydrolysis constants of the adsorbing metals. The user should ensure that hydrolysis constants in the thermodynamic data base are consistent with those used to determine adsorption constants. Numerous adsorption models are in use by researchers; their abundance is a reflection of their general inadequacy, and the model used here is no exception.

The model allows one to consider up to five surfaces simultaneously. Any number of metals and hydrolyzed metals may adsorb on any or all of the surfaces. This model does not include adsorption of ligands or metal-ligand complexes.

For each surface one must know the pH at which it carries no charge (pH_{ZPC}) and the constants for association with or loss of hydrogen ions. Surface concentrations of hydrogen exchange sites or surface complexes are given in moles of the species on surfaces in one liter of solution and will be denoted { }, while molar concentrations are denoted [ ]. Every surface HS can gain or lose H^+ :

$$H_2S^+ \longrightarrow H^+ + HS \qquad K^s_{a_1,app}$$

$$HS \longrightarrow H^+ + S^- \qquad K^s_{a_2,app}$$

so

$$\{S^-\} = K^s_{a_2,app}\{HS\}[H^+]^{-1}$$

and

$$\{H_2S^+\} = (K^s_{a_1,app})^{-1}\{HS\}[H^+]$$

The constants are apparent constants because they depend on the local electrical field at the surface which, in this work, is considered to be a function only of pH due to a Nernstian surface potential. Validity of this type of potential generally is limited to a narrow pH range about pH_{ZPC}. The apparent constants may be related to intrinsic constants by (in the following material, A and B will be used for alpha and beta which are most

commonly used in these equations)

$$K^s_{a_i,app} = K^s_{a_i,intr}\ 10^{A(pH_{ZPC} - pH)}$$

The constant A(alpha) is a scaling parameter (0-1) for the influence of the surface potential. The program requires intrinsic constants.

For metal adsorption or exchange of the types

$$M^{+z} + HS - H^+ \text{-->} MS^{z-1} \qquad {}^*K^s_{1,app}$$

and

$$M^{+z} + 2HS - 2H^+ \text{-->} MS_2^{z-2}\ {}^*B^s_{2,app}$$

the amounts of surface complexes formed are

$$\{MS^{z-1}\} = {}^*K^s_{1,app}\{HS\}[M^{z+}][H^+]^{-1}$$

and

$$\{MS_2^{z-2}\} = {}^*B^s_{2,app}\{HS\}^2[M^{z+}][H^+]^{-2}$$

The apparent constants are related to the intrinsic constants by

$${}^*K^s_{1,app} = {}^*K^s_{1,intr}\ 10^{(z-1)A(pH - pH_{ZPC})}$$

$${}^*B^s_{2,app} = {}^*B^s_{2,intr}\ 10^{(z-2)A(pH - pH_{ZPC})}$$

This theory assumes that the surface potential is not affected by adsorption of metal ions, which is a good assumption only when a small fraction of the surface sites are used in adsorption.

Because of the form of these equations, the complexes between surfaces and adsorbing metals can be treated just as other complexes in the program. The intrinsic constant is corrected to an apparent constant every time pH is modified during program execution. The constants (intrinsic and apparent) are very dependent on the ionic strength and also ionic medium and must be measured for each medium. These constants are not corrected within the program for changes in ionic strength.

As a brief example of typical data, Schindler et al. [9], found that for adsorption of Cu(II) on A-quartz (pH_{ZPC} = 2.0), $\log {}^*K^s_1$ = -8.3 and $\log {}^*B^s_2$ = -17.6 in 1M $NaClO_4$. These were apparent constants but appeared to be independent of pH so ${}^*K^s_{1,intr} = {}^*K^s_{1,intr}$ and A = 0.0. Schindler and Kamber [12] found that $\log K^s_{a_2,intr}$ = -6.8. This constant however will

definitely vary with pH and to use the constant A = 0, the user would probably want to calculate $K^s_{a_2,app}$ for each pH considered from the expression given above or from empirical expressions given by authors such as Schindler et al. [9], e.g.

$$\log (SiO^-) = 5.200 \log (-\log[H^+]) - 5.349$$

where (SiO^-) is the surface concentration moles per kg.

The formats for adsorption input data are shown in Table 2. The number of ligand surfaces is indicated in field 14 (column 42) of the Program Header Card (1). Data cards are required for each ligand surface. The cards, type (4), are included with the ligand input and contain the surface concentrations as moles of adsorbing sites per liter of solution (calculated from surface sites/kg and kg/l) for each case as well as a reference number (90-95) for the ligand. The other adsorption cards are placed at the end of the deck. There is one card of type (13) for each surface. It contains pH_{ZPC}, the intrinsic constant for loss of H^+, the intrinsic constant for gain of H^+ if given, the number of metals which can complex with the ligand, and A. Each metal requires a card of type (14) following the ligand surface card (13). The metal cards give the reference number of the metal, the number of complexes formed, the intrinsic constant, and stoichiometry (metal, ligand, and H^+) for each complex.

IV. PROGRAM OUTPUT

This section of the guide contains general descriptions of the standard output generated by the program. If only zeros are placed in fields 15 and 17-20 of the Program Header Card (1) the output for the program appears in eight printed formats. A ninth output showing interaction capacity and intensity is available and is called by placing 1, 2, or 3 in field 15 of the Program Header Card. These nine outputs are described below in order of appearance.

IV-A Program Introduction

This output gives the date and temperature of the data base used, the identification of the User Data Deck from card type (0), and error messages about the input deck. Disallowed solids also are listed. This output is shown in Figure B1B and B15B.

IV-B Thermodynamic Data for Verification

The second output routine presents the input thermodynamic data exactly as it comes from the Thermodynamic Data Deck but edited to retain only those constants applicable to the current computer run. For all possible formation reactions between species in the User Data Deck, the log of the formation constants and the stoichiometry of metals, ligands, hydrogen, and other components are given.

This type of output is repeated immediately after the User Input Data if the ionic strength is fixed. The constants shown here are corrected to the fixed ionic strength. When ionic strength is calculated, this output appears for each case immediately after the Final Ion and Solids Concentration output and gives the constants corrected to the computed ionic strength.

These outputs can be suppressed entirely by a 2 in field 20 of the Program Header Card. A 1 in field 20 allows only the uncorrected data to print. This output is shown in Figures B1C, B1E, B6B, and B15D.

IV-C User Input Data

This output describes the input data from the User Data Deck. All blanks on the User Data Deck are replaced by the numbers that will be used in the computation and this data should be checked carefully. A value of -0 which may be generated by some machines is the same as 0. Examples of this output are shown in Figures B1D, B2B, B6C, B7B, B8C, B10B, and B12B.

IV-D Case Progress

The output routine for Case Progress of the first case will follow the three routines above. After all of the other routines for the first case are printed, the program will print Case Progress for the second case, its following routines, Case Progress for the third case, etc. The Case Progress routine gives a brief outline of what is happening during successive program iterations for the current case. The number of times convergence for mass balance is reached by the program is shown. Every solid which precipitates or dissolves is listed. This only occurs after convergence for mass balance has been reached. When ionic strength is changed significantly or when total concentration(s) are changed to achieve balance, a message is printed. For cases with fixed pH the final charge on the solution is printed. The total concentration of the adjusted ion or the factor by which all ligand concentrations have been adjusted is listed if relevant. Execution error messages will appear here. Consult the error messages in Section V.

Examples of this output are shown in Figures B1F, B2C, B3B, B4B, B5B, B7F, B12C, B13D, B14C, B16C, and B18C.

IV-E Final Ion and Solid Concentrations

This output routine summarizes most of the results of the calculations. The pH, pOH, H^+ and OH^- concentrations are given. The total hydrogen less total hydroxide concentration is shown along with the soluble total hydrogen less total hydroxide (not in solids). The soluble alkalinity is given. pE, pCO_2, and pN_2 are shown when considered. The free concentrations and activities of all ions are listed. The total concentrations are shown, adjusted if they have been changed to obtain charge balance. If convergence has not been obtained after 200 iterations, the total concentrations may not be correct. The tabulated remainders have been used to measure convergence and, in general, are at least four orders of magnitude smaller than the total concentrations. Larger errors may be found for ions in solids or involved in ion-ion redoxes. The moles of solids precipitated from one liter of solution are shown, identified by their stoichiometries.

Examples of this output appear in Figures B1G, B2D, B3C, B4C, B5C, B6D, B7C-E, B7G, B7H, B8D-H, B9C-G, B10C, B11C, B12D, B13E, B14D, B15E, B16D, and B18D-H. B15b-d.

IV-F Saturation Ratios

Saturation Ratio output appears immediately after Final Ion and Solid Concentrations output or the corrected Themodynamic Data for Verification for each case. A 1 placed in field 17 of the Program Header Card will suppress this output. Sample outputs are shown in Figures B1G and B13F. They have

the same format as the formation constants for solids except that the log of the saturation ratio is shown. The saturation ratio is the ion product divided by K_{sp} for the solid:

$$SR = \frac{(M)^m(L)^l(H)^h}{K_{sp}} \qquad \text{for solid } M_mL_lH_h$$

The program prints -log(SR). A negative value of -log(SR) indicates supersaturation. An overflow number indicates that the solid has precipitated.

IV-G Concentration of Complexes

The Concentration of Complexes output follows the Saturation Ratios for each case. For each metal and ligand which form a complex, the metal, the ligand, -log M for the complex, and the stoichiometric coefficients of metal, ligand, and H^+ (OH^- if negative) are given.

If a 1 is placed in field 18 of the Program Header Card, this routine will also print the activity of each complex. A 1 in field 19 of the Program Header Card will suppress all Concentration of Complexes output.

An example of this output is shown in Figure B1G.

IV-H Primary Distributions of Metals and Ligands

The output for the Primary Distributions of Metals and Ligands shows the form (free, complexed, or in solid form with other species) and percentage of a metal or ligand which comprises more than 0.5 percent of the total concentration of that metal or ligand.

An example of this output is shown in Figure B1h.

IV-I Interaction Capacities and Intensities

This output, when called by 1, 2, or 3 in field 15 of the Program Header Card, will appear after the Concentration on Complexes output. The array elements for capacities are
$\partial pX/\partial TOTY$ and for intensities $\partial pX/\partial pTOTY$.

Total concentrations or log (total concentrations) are given in rows. Logs of free concentration are arrayed vertically. See Section III-N for details. The units for capacities are M^{-1}; intensities are unitless. Examples of this output are shown in figures B11D and B11E. Electrons are included only when pE is calculated.

V PROGRAM ERRORS

V-A Non-fatal Input Errors

These errors occur when input data is not self-consistent and thus the system under study may not be that which the user intended. These errors do not cause execution to stop at the time of detection; they may however lead to incorrect results or cause execution to fail at a later point. These error messages will be printed in the Program Introduction output. They are listed alphabetically below.

ATTEMPT TO IMPOSE, DISALLOW, OR CHECK SATURATION FOR SOLID __ OF M-L PAIR __ __ (reference numbers) WHICH IS NOT IN THE SYSTEM.

One of the ions making up the solid is missing. All components of the solid must be present in the metals and ligands. This solid cannot exist.

CANNOT INPUT ALKALINITY AND CALCULATE PH.

Total hydrogen and pH will be calculated incorrectly.

CANNOT VARY CONCENTRATION OF ION __ (reference number) AS IT IS NOT IN THE SYSTEM.

The ion chosen to vary for charge balance is not among the metals and ligands in the system. Charge balance will be ignored.

DO NOT CONSIDER N2 GAS WITH VARIABLE PE.

The imposition of N_2 gas implies a limitless supply of N_2. For variable pE, exact concentrations of each redox state must be known. Either fix pE or don't include $N_2(g)$ (redox reaction 2).

FOR PH FIXED, PE FIXED OR NOT CONSIDERED. FOR PH CALCULATED, PE NOT FIXED. DATA ON CARD 1, FIELDS 5 and 10 DO NOT AGREE.

The first two statements of this message are what should be true. Read Sections III-G and III-H if this message is not understood. Basically, pE should not be fixed if pH is not fixed, and pH should not be fixed while pE varies.

METAL __ (reference number) NOT IN DATA BASE. CANNOT ADSORB ON SURFACE __ (position of surface among all surfaces).

The information for adsorption of the metal whose reference number is given will be ignored. Add this metal if you wish to study its adsorption.

REACTION NUMBER __ (redox reaction number) SPECIFIED, BUT ONE OR MORE COMPONENTS MISSING.

All reactants and <u>products</u> (if an ion-ion redox) must be among the metal and ligands in the system. At least one is missing. Check that the

correct reaction was read from card type (10) and, if so, that all components are in the system. Total concentrations may be made very low.

THE THERMODYNAMIC DATA FILE DOES NOT CONTAIN ONE OR MORE OF THE METALS AND LIGANDS INPUT. THIS WILL CAUSE SEVERE PROBLEMS.
Compare the Thermodynamic Data File contents to the metals and ligands requested in the UDF.

THERE IS A FORMAT ERROR ON THE THERMODYNAMIC DATA FILE FOR REACTION __ (redox reaction number).
On the Thermodynamic Data Deck card for this reaction no ion was in field 2 and/or 3. If only one metal is involved and no ligand, use 99(OH^-) for the ligand. A missing metal should be represented by reference number 50 for H^+.

V-B Fatal Input Errors

Execution ceases upon occurrence of these errors. These messages will appear in the Program Introduction output. They are listed in alphabetical order.

CANNOT PRECIPITATE CO3 CONTAINING SOLID WHEN ALKALINITY INPUT.
Do not assume any solid containing CO_3^{2-} is present when carbonate alkalinity is given.

COLUMN 30 HEADER CARD MUST BE 0,1, OR 2. VALUE GIVEN WAS __.
The value of field 10 of the Program Header Card can only be 0, 1, or 2. Consult Sections III-G and III-H for the appropriate choice.

DON'T LET DISSOLVED O2 BE LESS THAN 1.0E-20 FOR ANY CASE.
Self-explanatory.

ERROR NUMBER __ (see next pages) OCCURRED IN ROUTINE __ (name of subroutine). THIS ERROR IS A PROGRAM ERROR AS EXPLAINED IN THE USERS MANUAL.
These errors occur when array bounds have been exceeded within the program. The errors are identified below by number.

Errors generated when program limits are exceeded:

201 Too many complexes were found for this system.
Remove a metal or ligand from the input data, remove complexes from the thermodynamic data, or increase the maximum number of complexes (750 is standard; MXC if parameter statement is used).

203 Too many mixed complexes were found for this system.
Remove a metal or ligand from the input data, remove mixed

complexes from the thermodynamic data, or increase the maximum number of mixed complexes (100 is standard; MCMIX if parameter statement is used).

205 Too many solids were found for this system. Remove a metal or ligand from the input data, remove solids from the thermodynamic data, or increase the maximum number of solids (100 is standard; MXS if parameter statement is used).

207 Too many redox reactions considered. Reduce the number of redox reactions on Card (10) of the User Data Deck or increase the maximum number of redox reactions (20 is standard; MXR if parameter statement is used).

212 Too many mixed solids in the Thermodynamic Data Deck. Reduce the number of mixed solids or increase the dimension of JDUM in subroutine INMIX and the loop on 68020. NTDF>60.

213 Too many mixed solids were found for this system. Remove a metal or ligand from the input data, remove mixed solids from the Thermodynamic Data Deck, or increase the maximum number of mixed solids (20 is standard; MXX if parameter statement is used).

215 Too many redox reactions in the Thermodynamic Data Deck. Reduce the number of reactions or increase the dimension of JDUM in subroutine INRED and the DO loop on 23020. NTDF>60. Most of the array sizes are set in the program parameter statement. This error occurs because too many thermodynamic data are available to the program for the system of metals and ligands given.

NO TOTAL CONCENTRATION FOR ION __ (position of a metal (H^+=1) or ligand among all metals and ligands in system) IN FIRST CASE.

A value for total concentration of this ion is needed for the first case.

NUMBER OF METALS, LIGANDS, OR CASES IS ZERO OR LESS.

The minimum number for metals, ligands, and cases is 1. Check that the correct columns are being used on the Program Header Card.

THERMODYNAMIC DATA BASE IS EMPTY OR MIS-POSITIONED.

The first line of the Thermodynamic Data Deck did not include the date. The deck is probably not there or not rewound properly.

TOO MANY METALS, LIGANDS, OR CASES. LIMITED TO ___.

The maximum number for metals, ligands or cases has been exceeded. Check that correct columns on the Program Header Card are being used.

USER INPUT CARD __ READ INSTEAD OF __.

The data deck was in correct order until this card was read. The deck may be scrambled or have too few or too many cards. If the card called for is missing, add it before the card numbered as shown on the left above. If the number read was lower than the number sought, there are too many cards; a card read was not needed. If the number read is 3 or 4 be sure there is one less Metal Card and one less Ligand Card than the numbers of metals and ligands shown on the Program Header Card.

V-C Non-Fatal Execution Errors

Upon occurrence of these errors, execution continues but the output may be less than satisfactory. These error messages will be printed in CASE PROGRESS. They are listed alphabetically below.

CO2 JUST DISSOLVED. THE TOTAL CO3 WAS NOT SUFFICIENT TO SATURATE THE SOLUTION WITH CO2 AT THIS PH. THIS SOLUTION IS NO LONGER AT EQUILIBRIUM WITH ANY CO2 IN THE ATMOSPHERE, UNLESS H2CO3 PRECIPITATES BELOW.

This message is self-explanatory. For further information see Section III-F.

CONCENTRATION OF ION __ (name) TOO SMALL TO ADJUST. MODIFY ALL LIGANDS TO ACHIEVE CHARGE BALANCE.

In order for charge to be balanced, the total concentration of the ion named would have to be negative. Since this is impossible, the ion is not adjusted. One can see whether it had been adjusted in previous iterations by checking the total concentration shown for it in the Final Ion and Solid Concentrations output.

NO CONVERGENCE AFTER ___ ITERATIONS

After the maximum number of iterations (200 standard) allowed, all the conditions for self-consistency among the program parameters have not been met. Convergence is near if the remainders in the Final Ion and Solid Concentrations output are orders of magnitude smaller than the total concentrations given in the User Input Data output and if the total concentrations (except for those in ion-ion redox) of these two outputs are nearly in agreement. Restart the calculation with the solids precipitated in this run present initially and the free concentration guesses set equal to the values shown in the last iteration. If some remainders are large and the total concentrations (actually total concentrations plus remainders) are large, something is wrong. Study Case Progress to see if something is repeatedly precipitating and dissolving. If so, disallow it. Simplify the case as

much as possible.

THE SOLUTION CHARGE IMBALANCE EXCEEDS 0.1 PERCENT OF THE IONIC STRENGTH. DO NOT USE THESE RESULTS FOR INPUT TO OTHER COMPUTER RUNS.

The total hydrogen calculated from these results will not be consistent with the known pH because the charge is not balanced. Some concentrations may also be incorrect because of errors in relative amounts of metals and ligands.

Z CANNOT BE INVERTED*

Correct interaction capacities and intensities will not be printed if the matrix ⟩TOTY/⟩ pX cannot be inverted because of a row or column which is null or which consists of elements which are very small relative to those in the other rows or columns. Execution may halt earlier if this problem arises.

V-D Fatal Execution Errors

Program execution ceases upon occurrence of these errors. All of the following occur because of solids or ion-ion redoxes. The easiest way to determine the nature of the problem is to simplify the case, then add complications until the problem reappears. These errors appear in CASE PROGRESS.

ATTEMPTED TO PRECIPITATE 3 SOLIDS FOR SAME METAL-LIGAND PAIR. DISALLOW ONE. LAST ATTEMPTED _____ (names of metal, ligand, and stoichiometries of metal, ligand and H^+).

Under certain pH conditions two or more solids containing the same metal-ligand pair can co-exist, e.g., $Ca_5(PO_4)_3OH$ and $CaHPO_4$. The program however is not set up to handle more than two co-existing solids involving the same metal-ligand pair. Two solids of this pair already existed (see initially assumed present solids and those which precipitate previously in CASE PROGRESS) when the program tried to precipitate a third, so execution stopped. Disallow the solid you think is least likely or assume different solids initially present.

CANNOT PRECIPITATE CO_3 CONTAINING SOLID WHEN ALKALINITY INPUT.

Disallow the CO_3^{2-} containing solid which just precipitated.

ERROR RETURN FROM GAUSSL, __TH DIAGONAL TERM REDUCED TO ZERO.

This error should not occur. Check input data carefully.

GIBBS PHASE RULE VIOLATION ASSOCIATED WITH
SOLID _____ (metal, ligand, stoichiometries)
or MIXED SOLID _____(name)
or ION-ION REDOX _____(name)

This error results from a closed family of connected solids. Everything depends on everything else and there is no free ion concentration left to be the independent variable. Some solid will have to be disallowed or an ion-ion redox omitted. The closed family of connected solids can probably be found by writing down all the precipitated solids and ion redoxes with ions in common with this solid or reaction. (Exclude those in common with H^+ if pH fixed and e- if pE fixed). Next, write down ions in common with any of the above solids and reactions. Repeat this until no more connected (sharing ion) solids and reactions can be found. When finished, there must be at least one more component (metal, ligand, H^+, and e-) than the number of solids and ion-ion redoxes. If not, the set of solids and reactions form a closed family of connected solids. An example might be $CaCO_3$, $MgCO_3$, and dolomite $CaMg(CO_3)_2$. This system has three components and three solids. Usually, but not always, one of these solids will dissolve before another precipitates. The case may work if a different solid(s) is assumed present initially.

VI THERMODYNAMIC DATA

VI-A Description of the Thermodynamic Data File

Formation (stability) constants at infinite dilution are required by the program. All reactions are written in terms of metals, ligands, protons, and electrons. The constants are input for the appropriate temperature and the temperature dependent constant for calculation of activity coefficients also is entered from the thermodynamic data deck. The constants are corrected to a fixed ionic strength (e.g., 0.5M) or ionic strength corrections can be made on the constants continuously while the program is running (see Section III-C). Either of two generalized activity coefficients can be used in correcting the constants (see Section III-M).

Equilibrium constants are stored as log K where K is the formation constant for a given solid or complex at infinite dilution. For solids, the log of the formation constant is the negative log of the solubility product. All formation reactions are written in terms of free metal ions, free ligands, and protons (H^+).

The format and variables for the thermodynamic data deck are listed and defined in Table 4. Examples of data lines from this deck are shown in Figure 5. The following text explains the deck and how to modify it. It is recommended that users examine the thermodynamic deck before using the program to determine whether complexes, solids, redox reactions, etc., in which they are interested are included in the data. Users are encouraged to create their own data files to suit their own needs or to change constants in order to make them consistent with other work. Card type numbers are used here for easy reference but are not included on the data card.

Table 4. Thermodynamic Data Deck Description

Card Type	Field(s)	Card Column(s)	Description
(0)			Deck Identification Card: 1 Card. Format 3A2,2X,F8.2.
	1	1-2	Month of the data deck.
	2	3-4	Day of the data deck.
	3	5-6	Year of the data deck.
	4	7-14	Temperature for which data will be read.
(1)			Metal and Ligand Header Card: 1 Card. Format 2I3,F7.2,F9.3.
	1	1-3	The number of metals including hydrogen for which data are available to the program.
	2	4-6	The number of ligands including hydroxide for which data are available to the program.
	3	7-13	Log K for the reaction $2H_2O \longrightarrow O_2(aq) + 4H^+ + 4e-$ with O_2 in mg/l.
	4	14-22	Correction factor for temperatures other than 25^oC for the term F/2.303RT where F is the Faraday constant, R the gas constant, and T is in ^oK.
(2)			Metal Cards: # cards = # metals given on header card, (1). Format 2I3,7X,F9.3,2X,A8.
	1	1-3	Reference number of metal. See Table 3.
	2	4-6	Charge of the metal.
	3	14-22	Atomic weight of metal in grams/mole.
	4	25-32	Identifying symbol for the metal.
(3)			Ligand Cards: # cards = # ligands given on header card, (1). Format 2I3,7X,F9.3,2X,A8

Table 4 (continued)

Card Type	Field	Card Columns	Description
	1	1-3	Reference number of ligand. See Table 3.
	2	4-6	Charge of ligand, including sign.
	3	14-22	Molecular weight of ligand in grams/mole.
	4	25-32	Identifying symbol for the ligand.
(4)			Solid and Complex Header Card: 1 Card. Format 3I5,I6
	1	1-5	Number of metal-ligand solid/complex cards to follow.
	2	6-10	100 x -log of the ionization constant of water = 14 at 0 ionic strength, T = 25°C.
	3	11-15	100 x log K of the equilibrium constant for the reaction: $2H^+ + CO_3^{2-} \longrightarrow CO_2(g) + H_2O$
	4	16-21	1000 X correction for temperature dependent constant for activity corrections when T is not equal to 25°C.
(5)			Solid and Complex Cards: # cards = 2 x # given on header card (4). Format A1,2I3,6(I5,2I2,I3) Cards must be in ascending numerical order for temperature adjustments.
	1	1	S or C for solids or complexes. Must have solids card first then complex card even if one is blank.
	2	2-4	Reference number of metal.
	3	5-7	Reference number of ligand combined with above metal.
	4	8-12	100 x log K where K is the formation constant of a solid or complex formed from the above metal, ligand, and hydrogen as H^+.
	5	13-14	Stoichiometric coefficient of the metal in the first solid or complex.

Table 4 (continued)

Card Type	Field	Card Columns	Description
	6	15-16	Stoichiometric coefficient of the ligand in the first solid or complex.
	7	17-19	Stoichiometric coefficient of hydrogen in the first solid or complex. (Negative number indicates number of OH^-.) Zero if neither present.
	8	20-24	Same as fields 4 through 7 except for a second solid or complex.
	9	25-26	
	10	27-28	
	11	29-31	
	12	32-36	Same as fields 4 through 7 except for a third solid or complex.
	13	37-38	
	14	39-40	
	15	41-43	
	16	44-48	Same as fields 4 through 7 except for a fourth solid or complex.
	17	49-50	
	18	51-52	
	19	53-55	
	20	56-60	Same as fields 4 through 7 except for a fifth solid or complex.
	21	61-62	
	22	63-64	
	23	65-67	
	24	68-72	Same as fields 4 through 7 except for a sixth solid or complex.
	25	73-74	
	26	75-76	
	27	77-79	
(6)			Redox Reaction Header Card: 1 card. Format I5.
	1	1-5	Number of redox reactions ($\leq$60).
(7)			Redox Reaction Cards: # cards = # given on header card (6). Format 6I5,I6,I4,I5,A8. Reactions must be in ascending numerical order for temperature adjustment.
	1	1-5	Arbitrary sequential number assigned to the redox reaction. See Appendix C. The first redox

Table 4 (continued)

Card Type	Field	Card Columns	Description
			reaction forming a solid must be assigned to: $2NO_3^- + 12H^+ \longrightarrow N_2(g) + 6H_2O - 10e-$
	2	6-10	Reference # of: metal to ligand; metal to metal; metal + ligand; ligand to ligand
	3	11-15	Reference # of: metal to ligand; metal to metal; metal + ligand; ligand to ligand
	4	16-20	Reaction type: -11; -10; -9 to -1 / 1 to 9; 10
			-11 is a metal oxidized/reduced to ligand. -10 is a metal oxidized/reduced to another metal. -9 to -1 is a metal + ligand forming a solid $\pm e-$. 1 to 9 is a metal + ligand forming a complex $\pm e-$. 10 is a ligand oxidized/reduced to another ligand.
	5	21-35	Number of e- produced (negative if consumed).
	6	26-30	Number of H^+ consumed (negative if produced).
	7	31-36	100 x log K for the reaction as written.
	8	37-40	Stoichiometric coefficient of ion given in field 2. Zero if metal 50.
	9	41-45	Stoichiometric coefficient of ion given in field 3. Zero if ligand 99.
	10	46-53	Name of the reaction, up to 8 alphanumeric characters.
(8)			Mixed Solid Header Card: 1 card. Format I4.
	1	1-4	Number of mixed solids for which data are available to the program ($\leq$60).
(9)			Mixed Solid Cards: # cards = # given on header card (8). Format 11I4,I6,2I4,A8. Solids must be in ascending numerical order for the temperature adjustment.

Table 4 (continued)

Card Type	Field	Card Columns	Description
	1	1-4	Arbitrary sequential number assigned to the mixed solid. See Appendix E.
	2	5-8	Reaction type: 0 if solid contains up to 2 metals and 2 ligands in addition to possible H^+ or OH^-. 1 if solid contains up to 4 metals in addition to Al^{3+} and $SiO_2(OH)_2^{2-}$.
	3	9-12	Reference number of first metal.
	4	13-16	Reference number of second metal. 50 if no second metal.
	5	17-20	Reference number of third metal for reaction type 1. Reference number of first ligand for reaction type 0. 50 if no third metal.
	6	21-24	Reference number of fourth metal for reaction type 1. Reference number of second ligand for reaction type 0. 50 if no fourth metal. 99 if no second ligand.
	7	25-28	Stoichiometric coefficient for ion in field 3.
	8	29-32	Stoichiometric coefficient for ion in field 4. Zero if no second metal.
	9	33-36	Stoichiometric coefficient for ion in field 5. Zero if no third metal.
	10	37-40	Stoichiometric coefficient for ion in field 6. Zero if no fourth metal or second ligand.
	11	41-44	Number of hydrogens in the solid (negative if hydroxide present). Do not count OH^- of $SiO_2(OH)_2^{2-}$.
	12	45-50	100 x log K where K is the formation constant of the reaction as written. See Appendix E.
	13	51-53	Number of Al^{3+} ions for type 1 reaction. Zero for type 0 reaction.

Table 4 (continued)

Card Type	Field	Card Columns	Description
	14	54-56	Number of $SiO_2(OH)_2^{2-}$ ions for type 1 reaction. Zero for type 0 reaction.
	15	57-64	Name of the mixed solid.
(10)			Mixed Complex Header Card Format 2I3
	1	1-3	Number of mixed complex cards.
	2	4-6	Number of mixed metal complex cards.
(11)			Mixed Complex Cards: # cards = # given on header card (10). Format 3I3,A1,5(I5,3I2,I3). For temperature adjustment, cards must be in ascending numerical order and all metal-metal-ligand complexes must follow metal-ligand-ligand complexes.
	1	1-3	Reference number of metal in mixed complex.
	2	4-6	Reference number of ligand in mixed complex.
	3	7-9	Reference number of third ion.
	4	10	Identifies third ion: M if a metal. L if a ligand.
	5	11-15	100 x log K for formation of the first mixed complex.
	6	16-17	Stoichiometry of metal in the first mixed complex.
	7	18-19	Stoichiometry of ligand in the first mixed complex.
	8	20-21	Stoichiometry of the third ion in the first mixed complex.
	9	22-24	Stoichiometry of H^+ (OH^- if negative) in the first mixed complex.
	10	25-29	100 x log K for formation of the second mixed complex.

Table 4 (continued)

Card Type	Field	Card Columns	Description
	11	30-31	Stoichiometry of metal in second mixed complex.
	12	32-33	Stoichiometry of ligand.
	13	34-35	etc., as for fields 8 and 9.
	14	36-38	
	15	39-43	Same as fields 5 through 9 except for third mixed complex.
	16	44-45	
	17	46-47	
	18	48-49	
	19	50-52	
	20	53-57	Same as fields 5 through 9 except for fourth mixed complex.
	21	58-59	
	22	60-61	
	23	62-63	
	24	64-66	
	25	67-71	Same as fields 5 through 9 except for fifth mixed complex.
	26	72-73	
	27	74-75	
	28	76-77	
	29	78-80	

VI-B Modification of the Thermodynamic Data File

1. Metals and ligands

The data deck must begin with an identifying card (0) which gives the date of creation and the temperature for which the constants are given. This card is shown in Figure 5.

Examples of the metal-ligand header card (1), a metal card (2), and a ligand card (3) are also shown in Figure 5. Card (1) shows that the thermodynamic deck includes information on 43 metals and 66 ligands. It also contains Sato's constant for calculation of pE from dissolved O_2 and a correction factor to F/2.303RT for conversion of Eh to pE at temperatures other than 25°C. (Zero since this deck is at 25°C; adds to 16.904). Card (2) says metal 23 (Be^{2+} from Table 1) has a charge of +2, an ionic radius of 0.35A, an atomic weight of 9.013 grams/mole, and will be identified as Be^{2+}. Sample card (3) says ligand 9 (PO_4^{3-}) has a charge equal to -3, ionic radius of 1.0A (if ionic radius is unknown, 1.0A is entered), molecular weight of 94.975 grams/mole, and will be identified as PO_4^{3-}. The ionic radius is not used by the version of the program described here.

If the user wishes to add more metals and ligands to the deck, this may be done by increasing the numbers on the header card and adding cards for metals 44 to 49 and ligands 67 to 89. Metals and ligands should not be renumbered or data in the data file for complexes, solids, etc. will be labeled incorrectly.

```
 0 021379  25.0
 1  36 63-11.385
 2  23  2   .35     9.013  BE  +2
 3   9 -3  1.00    94.975  PO4 -3
 4  1005 1400 1814
 5 S  2  1  746 1 1  0
 5 C  2  1  288 1 1  0 1128 1 1  1
 5 S  2 99-1684 1 0 -2
 6    22
 7    01   06   07  -10   -1   00  1300   1   1FE2/FE3
 7    02   50   57   -1  -10   12 20890   0   2N2(G)
 7    08   02    8   10   -8    8  2000   1   1SO4/S-2
 7    16   19   59  -11   03   -8 -7490   1   1CR3/CRO4
 8    6
 9    2   1   2   4  50  50   5  12         -20 13874  46  7OILLITE
 9    5   0   1   2   1  99   1   1   2   0       197   0    DOLOMITE
10  5
11  12  3  5L  191 1 3 1  0  215 1 2 2  0  275 1 1 3 0
```

Figure 5. Sample cards from the Thermodynamic Data Deck.

2. Complexes and solids

The next card, (4), after the metal and ligand cards, gives the number of pairs of cards on which solid and/or complex data will be given, the negative log of the ionization constant for water, 100 x log K for the reaction:

$$2\ H^+ + CO_3^{2-} = CO_2(g) + H_2O$$

and the temperature correction for the activity coefficient calculation (adds to 0.509). Specifically, card (4) in Figure 5 says:

Pairs of complexes/solids = 1005

$Kw = (H^+)\ (OH^-) = 10^{-14}$, and

$pCO_2/(H^+)^2(CO_3^{2-}) = 10^{18.14}$

Activity corr = 0 (25°C)

The solid and complex cards tell which solids and complexes can exist between a given metal and ligand. These solids and complexes are identified in the program output by the metals and the ligands they contain and their stoichiometries. In user input data they are identified by their order in the line(s) of data for that metal-ligand pair, e.g. as 1, 4, or 7 for the first, fourth, or seventh possible solid or as 1 through 10 for the first through tenth complexes. Cards of type (5) appear in pairs: the first for solids, the second for complexes. If all the data do not fit on one pair, a second pair of cards may be given for the same metal-ligand pair. Three examples of card (5) are shown. The first shows the solid of metal 2 (Mg^{2+}) and ligand 1 (CO_3^{2-}). One solid is shown which is formed according to:

$$1\ Mg^{2+} + 1\ CO_3^{2-} \longrightarrow MgCO_3(s) \qquad K = 10^{9.46}$$

The second card (5) shows the complexes for this metal ligand pair:

$$1\ Mg^{2+} + 1\ CO_3^{2-} \longrightarrow MgCO_3^{o} \qquad K = 10^{2.88}$$

$$1\ Mg^{2+} + 1\ CO_3^{2-} + 1\ H^+ \longrightarrow MgHCO_3^{+} \qquad K = 10^{11.28}$$

The final card (5) is a solid card for Mg^{2+} and OH^- reacting to form a solid

$$Mg^{2+} + 2\ H_2O \longrightarrow Mg(OH)_2(s) + 2\ H^+ \qquad K = 10^{-16.84}$$

In these solid and complex cards (5), additions, deletions, or modifications may be made on any card with no other changes in the data deck. No blank solid or complex slots should be left. Also a pair of data lines may be deleted or added and in that instance the total number of solid and complex lines in the data deck must be corrected on the header card (4).

3. Redox equations.

The number of redox reactions available follows the solid and complex data and is given on card (6). Each of these reactions is described on a redox card (7). The reactions currently on file are given in Appendix C.

For example, card (6) in Figure 5, says that 22 redox reactions are on file. Four examples of redox reactions are shown on cards (7). The first card (7) specifies that the first redox reaction (field 1) is of type -10 (field 4) with metal 6 (Fe^{3+}) (field 2) oxidized/reduced to metal 7 (Fe^{2+}) (field 3), with consumption of 1 electron (field 5) and no H^+ (field 6). Log K is 13.0 (field 7). Fields 8 and 9 indicate the reaction involves 1 Fe^{3+} and 1 Fe^{2+}.

$$Fe^{3+} + e- \longrightarrow Fe^{2+} \qquad K = (Fe^{2+})/(Fe^{3+})(e-) = 10^{13}$$

In the second card (7) reaction 2 is of type -1: 12 metal 50(H^+) and 2 ligand 57(NO_3) with 10e- form a solid (N_2 gas). The reaction is:

$$2\ NO_3^- + 12\ H^+ + 10\ e- \longrightarrow N_2(g) + 6\ H_2O \qquad K = 10^{208.9}$$

On the third card (7) reaction 8 is of type 10 so 1 ligand 8 (S^{2-}) is oxidized/reduced to 1 ligand 2 (SO_4^{2-}) producing 8 electrons and 8 H^+.

$$S^{2-} + 4\ H_2O \longrightarrow SO_4^{2-} + 8\ H^+ + 8\ e- \qquad K = 10^{-20.0}$$

The final redox reaction shown is a metal-ligand redox (type -11) with 1 metal 19 (Cr^{3+}) producing 1 ligand 59 (CrO_4^{2-}), 3 electrons and 8 H^+ according to:

$$Cr^{3+} + 4\ H_2O \longrightarrow CrO_4^{2-} + 8\ H^+ + 3\ e- \qquad K = 10^{-74.90}$$

For ion-ion redoxes, no ion should be both a reactant and a product (assuming all reactions written as reductions), although any one ion may be a participant in many reactions.

4. Mixed solids.

Mixed solids data appear after redox reactions. Their number is given on card type (8). Two mixed solid cards, type (9), are shown. The first is for illite, the second mixed solid (field 1), which is a clay (1 in field 2) and contains 5 (field 7) metal 2, Mg^{2+} (field 3), 12 (field 8) metal 4, K^+ (field 4), no other metals (only 50 in fields 5 and 6), 20 OH^- (field 11), 46 Al^{3+} (field 13) and 70 $SiO_2(OH)_2^{2-}$ (field 14). Thus the mixed solid is $Mg_5K_{11}Al_{46}(SiO_2(OH)_2)_{70}(OH)_{20}$ or 1/20 of this as shown in Appendix D, and log K = 1387.4. The second mixed solid shown (5, field 1), is of type 0 (field 2) and contains 1 (field 7) metal 1 (field 3), 1 (field 8) metal 2 (field 4), and 1 (field 9) ligand 1 (field 5).

More mixed solid cards may be added to a total of 60. The mixed solid header card (8) must be changed if mixed solids are added.

5. Mixed Complexes

The final information in the thermodynamic data deck is for mixed complexes. The number of cards of mixed complexes is given on card type (10). Each triplet requires one data card. More may be used if the triplet has more than five complexes. The data shown on card type (11) are for the triplet metal 12 (Zn^{2+}), ligand 3 (Cl^-), and ligand 5 (Br^-) (because followed by L). Three mixed complexes are formed:

$$Zn^{2+} + 3\ Cl^- + Br^- \longrightarrow ZnCl_3Br^{2-} \qquad K = 10^{1.91}$$

$$Zn^{2+} + 2\ Cl^- + 2\ Br^- \longrightarrow ZnCl_2Br_2^{\ 2-} \qquad K = 10^{2.15}$$

$$Zn^{2+} + Cl^- + 3\ Br^- \longrightarrow ZnCl_1Br_3^{\ -} \qquad K = 10^{2.75}$$

The format for mixed complexes is similar to that for complexes except for adding the stoichiometry for the third metal/ligand.

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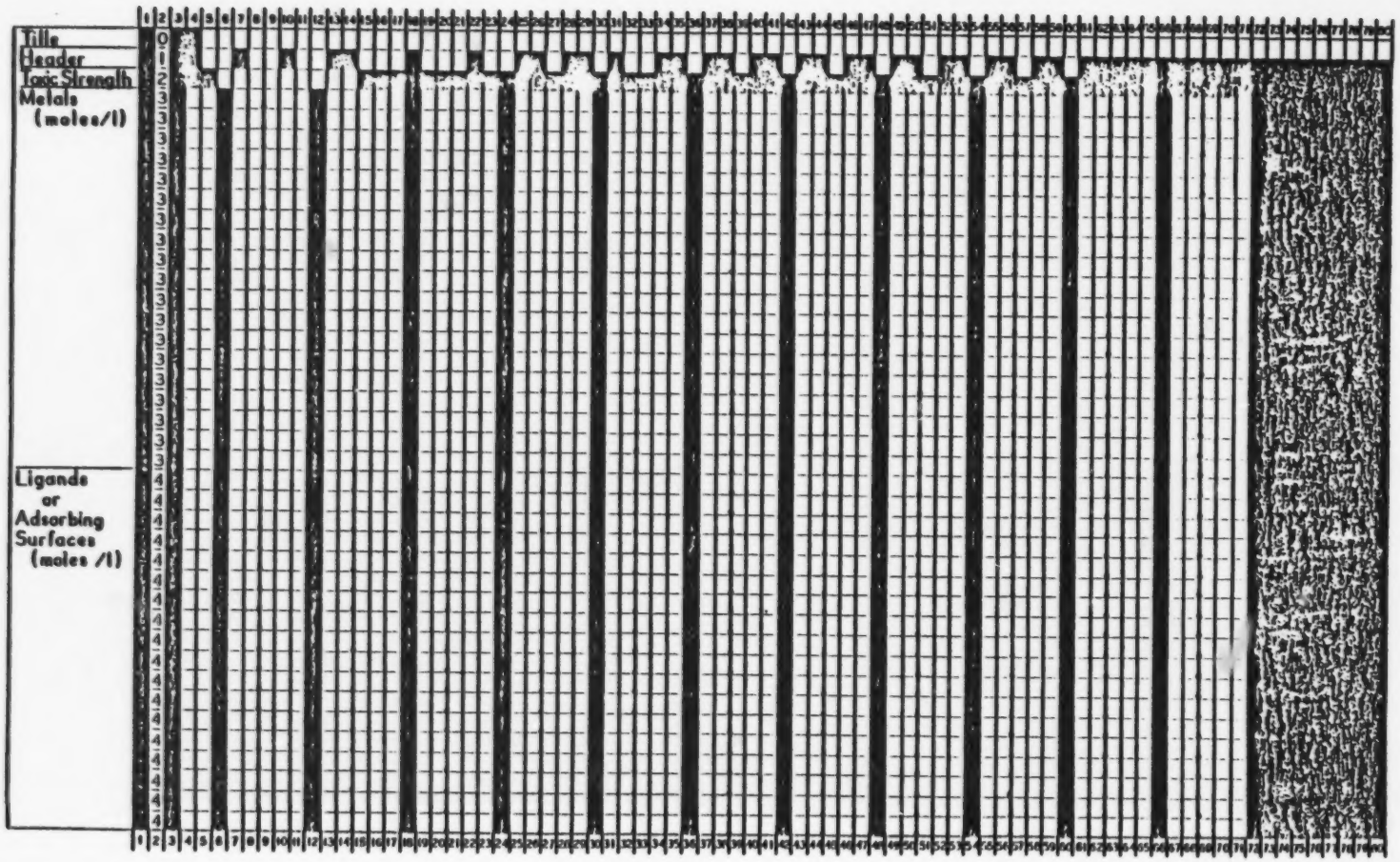
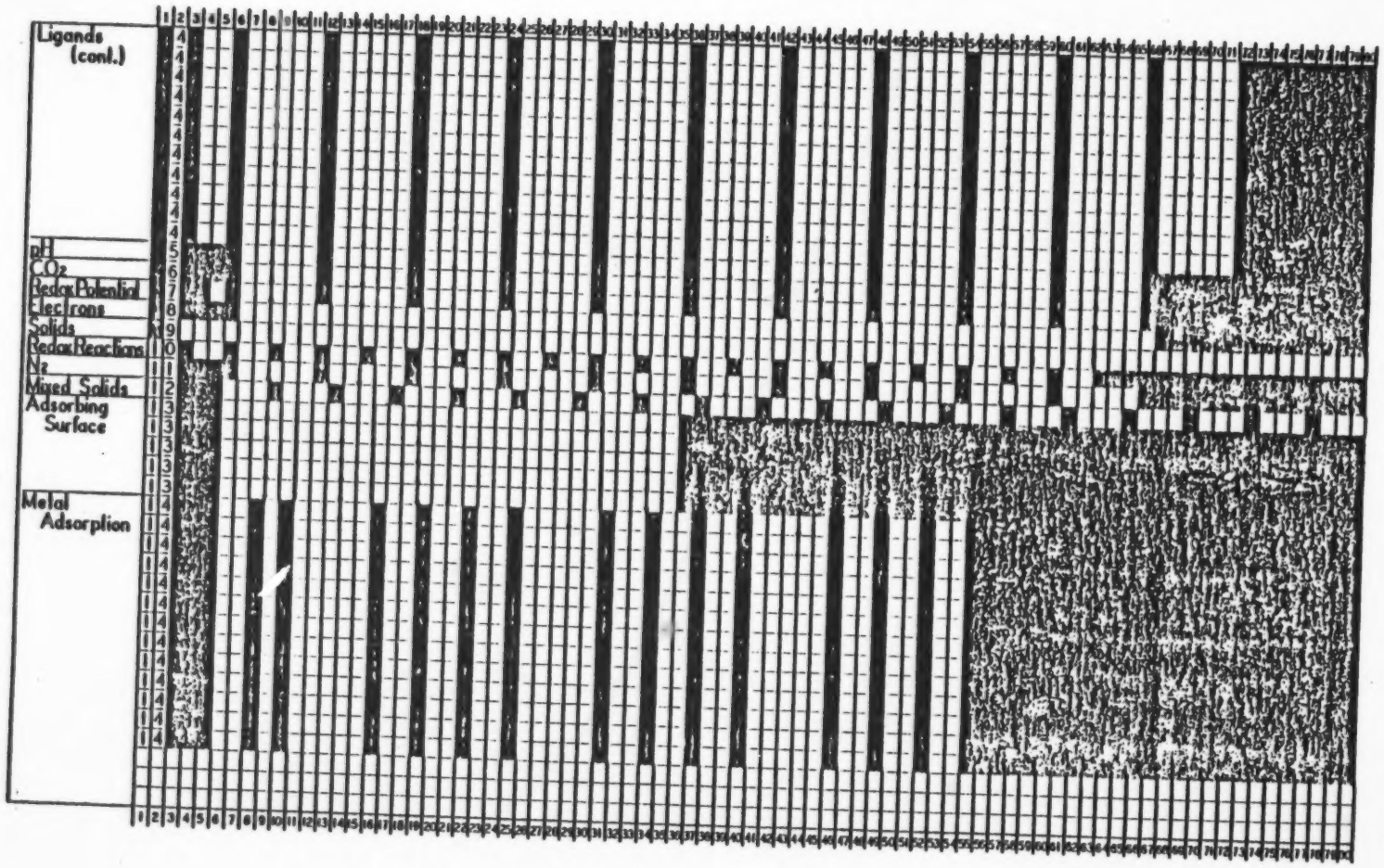
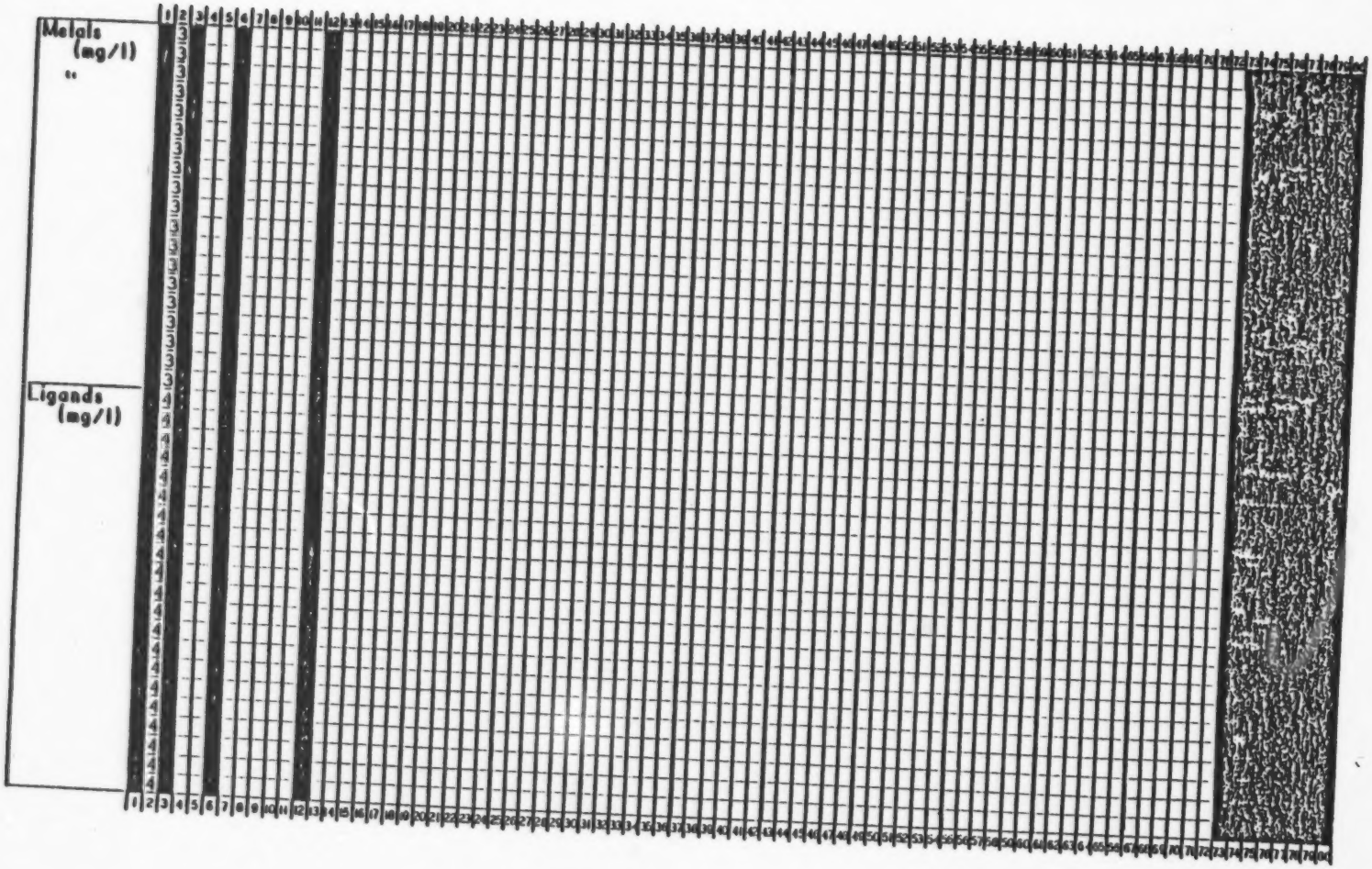
APPENDIX A

Sample Coding Sheets


Title
Header
Toxic Strength
Metals
(moles/l)
Ligands
or
Adsorbing
Surfaces
(moles /l)


Ligands (cont.)
pH
CO_2
Redox Potential
Electrons
Solids
Redox Reactions
N_2
Mixed Solids
Adsorbing Surface
Metal Adsorption


Metals (mg/l)
"
Ligands (mg/l)

APPENDIX B

Figures for Sample Output

FIGURE B1. UNDEQ--SAMPLE CALCULATION

FIGURE B1A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA
1    7  8  1
2       1.2E-03
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
```

FIGURE B1B.

```
U   U  M    M  OOOO   EEEEE   QQQ
U   U  MM MM  O   O  E      Q   Q
U   U  M M M  O   O  E      Q   Q
U   U  M   M  O   O  EEE    Q   Q
U   U  M   M  O   O  E      Q   Q
U   U  M   M  O   O  E      Q  QQ
 UUU   M   M  OOOO   EEEEE   QQQQ
```

UMDEQ VERSION 4.01.80

DATE 81/07/12. TIME 14.12.57.

USING THERMODYNAMIC DATA BASE OF 80/08/01
WHICH CONTAINS THERMODYNAMIC DATA FOR 25.00 DEGREES (C)

SHORT LAKE SUPERIOR DATA

FIGURE B1C.

UNCORRECTED THERMODYNAMIC DATA FOR VERIFICATION

CASE 1

SOLIDS

METAL	LIGAND	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
1 CA +2																									
	1 CO3 -2	8.37	1	1	0	8.31	1	1	0																
	2 SO4 -2	4.64	1	1	0	4.85	1	1	0																
	12 SIO3 -2	7.20	1	1	0																				
	99 OH -1	-22.81	1	0	-2																				
2 MG +2																									
	1 CO3 -2	7.46	1	1	0	4.67	1	1	0	4.54	1	1	0	-10.01	2	1	-2	8.77	5	4	-2				
	12 SIO3 -2	18.29	1	1	0	-6.68	2	1	-2	11.86	3	2	-2	63.43	3	4	2	48.95	2	3	2	46.08	2	3	2
	99 OH -1	-16.84	1	0	-2																				
5 NA +1																									
	1 CO3 -2	1.31	2	1	0	-.13	2	1	0	10.88	1	1	1	11.12	3	2	1								
	2 SO4 -2	.18	2	1	0	1.11	2	1	0																
	3 CL -1	-1.58	1	1	0																				
	12 SIO3 -2	165.64	1	7	13																				
6 FE +3																									
	99 OH -1	-3.20	1	0	-3	-.80	1	0	-3	4.01	2	0	-6	-6.39	2	0	-6								
12 ZN +2																									
	1 CO3 -2	10.00	1	1	0																				
	3 CL -1	-15.20	2	1	-3																				
	12 SIO3 -2	18.50	1	1	0																				
	99 OH -1	-12.50	1	0	-2	-11.33	1	0	-2	-11.75	1	0	-2	-11.79	1	0	-2	-11.73	1	0	-2	-11.84	1	0	-2
19 CR +3		-11.53	1	0	-2																				
	99 OH -1	-11.00	1	0	-3																				
51 H +1																									
	12 SIO3 -2	25.74	0	1	2	26.48	0	1	2	26.55	0	1	2	26.97	0	1	2								

COMPLEXES

METAL	LIGAND	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
1 CA +2																									
	1 CO3 -2	3.15	1	1	0	11.33	1	1	1																
	2 SO4 -2	2.31	1	1	0																				
	12 SIO3 -2	3.09	1	1	0	13.50	1	1	1	29.10	1	2	2												
	57 NO3 -1	.70	1	1	0	.60	1	2	0																
	99 OH -1	-12.85	1	0	-1																				
2 MG +2																									
	1 CO3 -2	2.88	1	1	0	11.28	1	1	1																
	2 SO4 -2	2.23	1	1	0																				
	3 CL -1	-1.00	1	1	0																				
	12 SIO3 -2	4.17	1	1	0	13.70	1	1	1	30.00	1	2	2												
	99 OH -1	-11.44	1	0	-1	-39.71	4	0	-4																
5 NA +1																									
	1 CO3 -2	1.20	1	1	0																				
	2 SO4 -2	.70	1	1	0																				
	3 CL -1	-1.85	1	1	0																				

```
         67 NO3 -1       -.60  1  1   0
         99 OH -1      -14.18  1  0  -1
6 FE +3
          2 SO4 -2       4.04  1  1   0     5.38  1  2   0
          3 CL -1        1.48  1  1   0     2.13  1  2   0     1.30  1  3   0
          6 I  -1        3.50  1  1   0     2.40  1  2   0
         12 SIO3 -2     22.60  1  1   1
         57 NO3 -1       1.00  1  1   0
         59 CRO4 -2      7.81  1  1   0
         99 OH -1       -2.19  1  0  -1    -5.67  1  0  -2   -21.60  1  0  -4    -2.95  2  0  -2    -6.35  3  0  -4
12 ZN +2
          1 CO3 -2       4.70  1  1   0                         1.70  1  3   0     1.70  1  4   0
          2 SO4 -2       2.38  1  1   0     3.20  1  2   0      .50  1  3   0      .20  1  4   0
          3 CL -1         .43  1  1   0      .61  1  2   0    -1.83  1  3   0    -2.42  1  4   0
          6 I  -1       -1.50  1  1   0    -1.76  1  2   0
         57 NO3 -1        .40  1  1   0     -.30  1  2   0
         99 OH -1       -8.96  1  0  -1   -28.40  1  0  -3   -41.20  1  0  -4   -16.90  1  0  -2    -9.00  2  0  -1
19 CR +3
          2 SO4 -2       2.70  1  1   0
          3 CL -1         .80  1  1   0      .01  1  2   0
         99 OH -1       -4.00  1  0  -1    -9.70  1  0  -2   -27.40  1  0  -4    -5.06  2  0  -2    -8.15  3  0  -4   -18.90  1  0  -3
53 H  +1
          1 CO3 -2      10.33  0  1   1    16.68  0  1   2
          2 SO4 -2       1.99  0  1   1
         12 SIO3 -2     13.10  0  1   1    23.00  0  1   2    55.90  0  4   4    78.20  0  4   6
         59 CRO4 -2      6.51  0  1   1    14.55  0  2   2     6.31  0  1   2


MIXED COMPLEXES
---------------
MET      LIG      ION3       LOG K M  L I3  H   LOG K M  L I3  H   LOG K M  L I3  H   LOG K M  L I3  H   LOG K M  L I3  H
---      ---      ----       ----------------   ----------------   ----------------   ----------------   ----------------
ZN +2    CL -1    I  -1       .99  1  2  1  0    .69  1  1  2  0   1.51  1  3  1  0   1.11  1  2  2  0
```

FIGURE B1D.

USER INPUT DATA

CASE 1

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 45 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-03

THE CONDITIONS FOR THE 1 CASES ARE

	NUMBER	TOTAL CONCENTRATIONS CASE 1
-LOG(MOLES/L)		
METALS		
CA +2	1	3.500
MG +2	2	4.600
NA +1	5	4.300
FE +3	6	7.300
ZN +2	12	6.800
CR +3	19	8.400
LIGANDS		
CO3 -2	1	3.100
SO4 -2	2	4.500
CL -1	3	4.400
I -1	6	8.100
SIO3 -2	12	4.400
NO3 -1	57	4.700
CRO4 -2	59	12.800
FIXED PH		7.950

FIGURE B1E.

THERMODYNAMIC DATA AFTER IONIC STRENGTH CORRECTIONS WITH MAGNUSON EQUATION. CASE 1

SOLIDS

METAL	LIGAND	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
1 CA +2																									
	1 CO3 -2	8.24	1	1	0	8.18	1	1	0																
	2 SO4 -2	4.51	1	1	0	4.72	1	1	0																
	12 SIO3 -2	7.07	1	1	0																				
	99 OH -1	-22.84	1	0	-2																				
2 MG +2																									
	1 CO3 -2	7.33	1	1	0	4.54	1	1	0	4.41	1	1	0	-10.18	2	1	-2	8.20	5	4	-2				
	12 SIO3 -2	10.16	1	1	0	-6.85	2	1	-2	10.76	3	2	-2	62.93	3	4	2	48.58	2	3	2	45.71	2	3	2
	99 OH -1	-16.87	1	0	-2																				
5 NA +1																									
	1 CO3 -2	1.21	2	1	0	-.23	2	1	0	10.78	1	1	1	10.92	3	2	1								
	2 SO4 -2	.08	2	1	0	1.01	2	1	0																
	3 CL -1	-1.61	1	1	0																				
	12 SIO3 -2	164.94	1	7	13																				
6 FE +3																									
	99 OH -1	-3.30	1	0	-3	-.90	1	0	-3	3.81	2	0	-6	-6.59	2	0	-6								
12 ZN +2																									
	1 CO3 -2	9.87	1	1	0																				
	3 CL -1	-15.30	2	1	-3																				
	12 SIO3 -2	18.37	1	1	0																				
	99 OH -1	-12.53	1	0	-2	-11.36	1	0	-2	-11.78	1	0	-2	-11.82	1	0	-2	-11.76	1	0	-2	-11.87	1	0	-2
19 CR +3		-11.56	1	0	-2																				
	99 OH -1	-11.10	1	0	-3																				
-50 H +1																									
	12 SIO3 -2	25.64	0	1	2	26.38	0	1	2	26.45	0	1	2	26.87	0	1	2								

COMPLEXES

METAL	LIGAND	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
1 CA +2																									
	1 CO3 -2	3.02	1	1	0	11.20	1	1	1																
	2 SO4 -2	2.18	1	1	0																				
	12 SIO3 -2	2.96	1	1	0	13.37	1	1	1	28.87	1	2	2												
	57 NO3 -1	.63	1	1	0	.56	1	2	0																
	99 OH -1	-12.88	1	0	-1																				
2 MG +2																									
	1 CO3 -2	2.75	1	1	0	11.15	1	1	1																
	2 SO4 -2	2.10	1	1	0																				
	3 CL -1	-1.07	1	1	0																				
	12 SIO3 -2	4.04	1	1	0	13.57	1	1	1	29.77	1	2	2												
	99 OH -1	-11.47	1	0	-1	-39.64	4	0	-4																
5 NA +1																									
	1 CO3 -2	1.13	1	1	0																				
	2 SO4 -2	.63	1	1	0																				
	3 CL -1	-1.88	1	1	0																				

	57 NO3 -1	-.63	1	1	0																				
	99 OH -1	-14.18	1	0	-1																				
6 FE +3																									
	2 SO4 -2	3.84	1	1	0	5.11	1	2	0																
	3 CL -1	1.38	1	1	0	1.96	1	2	0	1.10	1	3	0												
	6 I -1	3.40	1	1	0	2.23	1	2	0																
	12 SIO3 -2	22.43	1	1	1																				
	57 NO3 -1	.90	1	1	0																				
	59 CRO4 -2	7.61	1	1	0																				
	99 OH -1	-2.26	1	0	-1	-5.77	1	0	-2	-21.67	1	0	-4	-2.95	2	0	-2	-6.27	3	0	-4				
12 ZN +2																									
	1 CO3 -2	4.57	1	1	0																				
	2 SO4 -2	2.25	1	1	0	3.07	1	2	0	1.70	1	3	0	1.97	1	4	0								
	3 CL -1	.36	1	1	0	.51	1	2	0	.40	1	3	0	.13	1	4	0								
	6 I -1	-1.57	1	1	0	-1.86	1	2	0	-1.93	1	3	0	-2.49	1	4	0								
	57 NO3 -1	.33	1	1	0	-.40	1	2	0																
	99 OH -1	-8.99	1	0	-1	-28.40	1	0	-3	-41.13	1	0	-4	-16.93	1	0	-2	-8.97	2	0	-1				
19 CR +3																									
	2 SO4 -2	2.50	1	1	0																				
	3 CL -1	.70	1	1	0	-.16	1	2	0																
	99 OH -1	-4.07	1	0	-1	-9.80	1	0	-2	-27.47	1	0	-4	-5.06	2	0	-2	-8.12	3	0	-4	-18.15	1	0	-3
50 H +1																									
	1 CO3 -2	10.26	0	1	1	16.58	0	1	2																
	2 SO4 -2	1.92	0	1	1																				
	12 SIO3 -2	13.03	0	1	1	22.90	0	1	2	55.83	0	4	4	77.90	0	4	6								
	59 CRO4 -2	6.44	0	1	1	14.45	0	2	2	6.21	0	1	2												

MIXED COMPLEXES

MET	LIG	ION3	LOG K	M	L	I3	H	LOG K	M	L	I3	H	LOG K	M	L	I3	H	LOG K	M	L	I3	H	LOG K	M	L	I3	H
ZN +2	CL -1	I -1	.89	1	2	1	0	.59	1	1	2	0	1.44	1	3	1	0	1.04	1	2	2	0					

FIGURE B1F.

CASE NUMBER 1


```
CASE PROGRESS
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  17 ITERATIONS.
SOLID  FE +3    OH -1     2 0-6  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  18 ITERATIONS.
SOLID  ZN +2    SIO3 -2   1 1 0  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  21 ITERATIONS.

  CHARGE ON SOLUTION (MOLES/LITER) = -2.230E-05

    THE SOLUTION CHARGE IMBALANCE EXCEEDS 0.1 PERCENT* OF THE IONIC STRENGTH.
DO NOT USE THESE RESULTS FOR INPUT TO OTHER COMPUTER RUNS.
```

FIGURE B1G.

CASE 1

FINAL ION AND SOLID CONCENTRATIONS

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.859E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.816E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	1.232E-16
2	MG +2	9.882E-05	4.005	8.475E-05	4.072	1.000E-04	4.000	6.330E-17
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-3.389E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.180E-07	6.928	1.012E-07	6.995	1.585E-07	6.800	-1.582E-11
19	CR +3	2.354E-15	14.628	1.665E-15	14.779	3.981E-09	8.400	1.191E-22
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	4.337E-17
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	-2.050E-19
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-6.422E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	-8.936E-24
12	SIO3 -2	3.646E-12	11.438	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.993E-05	4.701	1.918E-05	4.717	1.995E-05	4.700	5.075E-20
59	CRO4 -2	9.687E-13	12.014	8.367E-13	12.081	1.000E-12	12.000	-1.249E-27

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	3.874E-09

SATURATION OF SOLIDS

CASE 1

SP = IONIZATION PRODUCT X FORMATION CONSTANT. ***** INDICATES PRECIPITATION.

SOLIDS METAL	LIGAND	LOG 1/SP	M	L	H	LOG 1/SP	M	L	H	LOG 1/SP	M	L	H	LOG 1/SP	M	L	H	LOG 1/SP	M	L	H	LOG 1/SP	M	L	H
1 CA +2																									
	1 CO3 -2	.71	1	1	0	.77	1	1	0																
	2 SO4 -2	3.52	1	1	0	3.31	1	1	0																
	12 SIO3 -2	7.88	1	1	0																				
	99 OH -1	10.48	1	0	-2																				
2 MG +2																									
	1 CO3 -2	2.12	1	1	0	4.91	1	1	0	5.04	1	1	0	7.76	2	1	-2	17.73	5	4	-2				
	12 SIO3 -2	5.29	1	1	0	10.43	2	1	-2	8.27	3	2	-2	10.71	3	4	2	9.61	2	3	2	12.48	2	3	2
	99 OH -1	5.81	1	0	-2																				
5 NA +1																									
	1 CO3 -2	12.83	2	1	0	14.27	2	1	0	6.98	1	1	1	20.88	3	2	1								
	2 SO4 -2	13.05	2	1	0	12.12	2	1	0																
	3 CL -1	10.31	1	1	0																				
	12 SIO3 -2	22.56	1	7	13																				
6 FE +3																									
	99 OH -1	5.28	1	0	-3	2.80	1	0	-3	*******	2	0	-6	10.40	2	0	-6								
12 ZN +2																									
	1 CO3 -2	2.51	1	1	0																				
	3 CL -1	9.76	2	1	-3																				
	12 SIO3 -2	*******	1	1	0																				
	99 OH -1	3.68	1	0	-2	2.43	1	0	-2	2.85	1	0	-2	2.89	1	0	-2	2.83	1	0	-2	2.94	1	0	-2
19 CR +3		2.63	1	0	-2																				
	99 OH -1	1.93	1	0	-3																				
50 H +1																									
	12 SIO3 -2	1.66	0	1	2	.92	0	1	2	.85	0	1	2	.43	0	1	2								

CONCENTRATIONS OF COMPLEXES

CASE 1

METAL	LIGAND	CONC -LOG(M)	M	L	H	CONC -LOG(M)	M	L	H	CONC -LOG(M)	M	L	H	CONC -LOG(M)	M	L	H	CONC -LOG(M)	M	L	H	CONC -LOG(M)	M	L	H
1 CA +2																									
	1 CO3 -2	5.93	1	1	0	5.69	1	1	1																
	2 SO4 -2	5.86	1	1	0																				
	12 SIO3 -2	11.99	1	1	0	9.51	1	1	1	13.38	1	2	2												
	57 NO3 -1	7.57	1	1	0	12.41	1	2	0																
	99 OH -1	8.46	1	0	-1																				
2 MG +2																									
	1 CO3 -2	6.70	1	1	0	6.24	1	1	1																
	2 SO4 -2	6.43	1	1	0																				
	3 CL -1	9.47	1	1	0																				
	12 SIO3 -2	11.41	1	1	0	9.81	1	1	1	12.98	1	2	2												
	99 OH -1	7.55	1	0	-1	23.93	4	0	-4																
5 NA +1																									
	1 CO3 -2	8.61	1	1	0																				
	2 SO4 -2	8.19	1	1	0																				
	3 CL -1	10.58	1	1	0																				
	57 NO3 -1	9.63	1	1	0																				
	99 OH -1	10.55	1	0	-1																				
6 FE +3																									
	2 SO4 -2	26.39	1	1	0	29.64	1	2	0																
	3 CL -1	28.72	1	1	0	32.54	1	2	0	37.80	1	3	0												
	6 I -1	30.40	1	1	0	39.67	1	2	0																
	12 SIO3 -2	22.64	1	1	1																				
	57 NO3 -1	29.51	1	1	0																				
	59 CRO4 -2	30.11	1	1	0																				
	99 OH -1	20.03	1	0	-1	15.61	1	0	-2	15.64	1	0	-4	38.49	2	0	-2	51.65	3	0	-4				
12 ZN +2																									
	1 CO3 -2	7.81	1	1	0																				
	2 SO4 -2	9.21	1	1	0	12.91	1	2	0	18.80	1	3	0	23.06	1	4	0								
	3 CL -1	10.97	1	1	0	15.22	1	2	0	19.73	1	3	0	24.39	1	4	0								
	6 I -1	16.60	1	1	0	24.99	1	2	0	33.16	1	3	0	41.81	1	4	0								
	57 NO3 -1	11.30	1	1	0	16.73	1	2	0																
	99 OH -1	7.99	1	0	-1	11.53	1	0	-3	16.33	1	0	-4	8.00	1	0	-2	14.89	2	0	-1				
19 CR +3																									
	2 SO4 -2	16.65	1	1	0																				
	3 CL -1	18.33	1	1	0	23.59	1	2	0																
	99 OH -1	16.76	1	0	-1	8.56	1	0	-2	10.36	1	0	-4	18.45	2	0	-2	20.27	3	0	-4	8.93	1	0	-3
53 H +1																									
	1 CO3 -2	3.11	0	1	1	4.73	0	1	2																
	2 SO4 -2	10.54	0	1	1																				
	12 SIO3 -2	6.34	0	1	1	4.41	0	1	2	21.65	0	4	4	15.45	0	4	6								
	59 CRO4 -2	13.50	0	1	1	25.44	0	2	2	21.67	0	1	2												

MIXED COMPLEXES

MET	LIG	IONS	CONC -LOG(M)	M	L	IS	H	CONC -LOG(M)	M	L	IS	H	CONC -LOG(M)	M	L	IS	H	CONC -LOG(M)	M	L	IS	H	CONC -LOG(M)	M	L	IS	H
ZN +2	CL -1	I -1	22.94	1	2	1	0	26.94	1	1	2	0	26.78	1	3	1	0	30.68	1	2	2	0					

FIGURE B1H.

PRIMARY DISTRIBUTION OF METAL SPECIES
AS PERCENTS OF THEIR TOTAL CONCENTRATIONS.
PERCENTS GREATER THAN .50 ARE SHOWN.

CASE 1

CA +2

98.5	AS A FREE METAL
1.0	COMPLEXED WITH CO3 -2

MG +2

98.8	AS A FREE METAL
.8	COMPLEXED WITH CO3 -2

NA +1

100.0	AS A FREE METAL

FE +3

100.0	IN SOLID FORM WITH OH -1

ZN +2

74.4	AS A FREE METAL
9.9	COMPLEXED WITH CO3 -2
2.4	IN SOLID FORM WITH SIO3 -2
12.9	COMPLEXED WITH OH -1

CR +3

100.0	COMPLEXED WITH OH -1

PRIMARY DISTRIBUTION OF LIGAND SPECIES
AS PERCENTS OF THEIR TOTAL CONCENTRATIONS.
PERCENTS GREATER THAN .50 ARE SHOWN.

CASE 1

CO3 -2

99.0 COMPLEXED WITH H +1

SO4 -2

94.4 AS A FREE LIGAND
4.4 COMPLEXED WITH CA +2
1.2 COMPLEXED WITH MG +2

CL -1

100.0 AS A FREE LIGAND

I -1

100.0 AS A FREE LIGAND

SIO3 -2

100.0 COMPLEXED WITH H +1

NO3 -1

99.9 AS A FREE LIGAND

CRO4 -2

96.9 AS A FREE LIGAND
3.1 COMPLEXED WITH H +1

FIGURE B2. UNDEQ--CALCULATION INVOLVING VARIABLE IONIC STRENGTH

FIGURE B2A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH IONIC STRENGTH CHANGING
1   7  8  1  0  1
3  1  55     35
3  2  60     40
3  5  63     43
3  6  93     73
3 12  88     68
3 19 104     84
4  1  51     31
4  2  65     45
4  3  64     44
4  6 101     81
4 12  64     44
4 57  67     47
4 59 140    120
5     795
```

FIGURE 82B.

USER INPUT DATA

CASE 3

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 45 POSSIBLE SOLIDS.

IONIC STRENGTH WILL BE CALCULATED.

THE CONDITIONS FOR THE 1 CASES ARE

	NUMBER	TOTAL CONCENTRATIONS CASE 1
-LOG(MOLES/L)		
METALS		
CA +2	1	3.500
MG +2	2	4.000
NA +1	5	4.300
FE +3	6	7.300
ZN +2	12	6.800
CR +3	19	8.400
LIGANDS		
CO3 -2	1	3.100
SO4 -2	2	4.500
CL -1	3	4.400
I -1	6	8.100
SIO3 -2	12	4.400
NO3 -1	57	4.700
CRO4 -2	59	12.000
FIXED PH		7.950

FIGURE B2C.

CASE NUMBER 1

CASE 1

```
CASE PROGRESS
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  18 ITERATIONS.
SOLID  FE +3    OH -1      2 0-6  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  19 ITERATIONS.
SOLID  ZN +2    SIO3 -2    1 1 0  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  23 ITERATIONS.
IONIC STRENGTH CHANGED.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  27 ITERATIONS.

  CHARGE ON SOLUTION (MOLES/LITER) = -2.234E-05

    THE SOLUTION CHARGE IMBALANCE EXCEEDS 0.1 PERCENT* OF THE IONIC STRENGTH.
DO NOT USE THESE RESULTS FOR INPUT TO OTHER COMPUTER RUNS.
```

FIGURE 82D.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.329E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.859E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.860E-04
-LOG KW = 13.965
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.817E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.653E-04	3.576	3.162E-04	3.500	7.144E-17
2	MG +2	9.884E-05	4.005	8.414E-05	4.075	1.010E-04	4.000	3.680E-17
5	NA +1	5.011E-05	4.300	4.814E-05	4.317	5.012E-05	4.300	3.519E-21
6	FE +3	1.779E-26	25.750	1.238E-26	25.907	5.012E-08	7.300	0
12	ZN +2	1.180E-07	6.925	1.011E-07	6.995	1.585E-07	6.800	-9.227E-12
19	CR +3	2.390E-15	14.622	1.663E-15	14.779	3.981E-09	8.400	-8.537E-22
1	CO3 -2	3.614E-06	5.442	3.077E-06	5.512	7.943E-04	3.100	-3.437E-17
2	SO4 -2	2.988E-05	4.525	2.543E-05	4.595	3.162E-05	4.500	4.323E-20
3	CL -1	3.981E-05	4.400	3.825E-05	4.417	3.981E-05	4.400	6.741E-21
6	I -1	7.943E-09	8.100	7.631E-09	8.117	7.943E-09	8.100	2.470E-23
12	SIO3 -2	3.672E-12	11.435	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.993E-05	4.701	1.914E-05	4.718	1.995E-05	4.700	3.724E-20
59	CRO4 -2	9.688E-13	12.014	8.248E-13	12.084	1.000E-12	12.000	2.786E-27

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	3.032E-09

FIGURE B3. UMDEQ--CHARGE ADJUSTMENT BY VARYING ALL IONS

FIGURE B3A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA ADJUSTED FOR SOLUTION CHARGE
1    7  8  1  0  1100
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
```

FIGURE B3B.

CASE NUMBER 1 CASE 1

```
CASE PROGRESS
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  18 ITERATIONS.
SOLID  FE +3    OH -1     2 8-6  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  19 ITERATIONS.
SOLID  ZN +2    SIO3 -2   1 1 0  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  23 ITERATIONS.
IONIC STRENGTH CHANGED.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  27 ITERATIONS.
CHARGE ON THE SOLUTION ADJUSTED.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  30 ITERATIONS.
CHARGE ON THE SOLUTION ADJUSTED.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  32 ITERATIONS.
SOLID  ZN +2    SIO3 -2   1 1 0  DISSOLVES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  34 ITERATIONS.
CHARGE ON THE SOLUTION ADJUSTED.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  36 ITERATIONS.
CHARGE ON THE SOLUTION ADJUSTED.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  38 ITERATIONS.
CHARGE ON THE SOLUTION ADJUSTED.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  40 ITERATIONS.

  CHARGE ON SOLUTION (MOLES/LITER) = -6.650E-07
 LIGAND TOTAL CONCENTRATIONS ADJUSTED BY A FACTOR OF   .976
```

FIGURE 03C.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.318E-03

FIXED PH = 7.950 POH = 6.050

COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.646E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.648E-04

-LOG KW = 13.965

H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033

CARBONATE ALKALINITY = 7.630E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.117E-04	3.506	2.654E-04	3.576	3.162E-04	3.500	-3.756E-14
2	MG +2	9.886E-05	4.005	8.416E-05	4.075	1.000E-04	4.000	-7.262E-15
5	NA +1	5.011E-05	4.300	4.814E-05	4.317	5.012E-05	4.300	-9.444E-19
6	FE +3	1.779E-26	25.750	1.238E-26	25.907	5.012E-08	7.300	0
12	ZN +2	1.214E-07	6.916	1.034E-07	6.986	1.585E-07	6.800	-9.751E-16
19	CR +3	2.390E-15	14.622	1.603E-15	14.779	3.981E-09	8.400	4.963E-22
1	CO3 -2	3.527E-06	5.453	3.003E-06	5.522	7.753E-04	3.111	-3.193E-14
2	SO4 -2	2.916E-05	4.535	2.482E-05	4.605	3.086E-05	4.511	-1.362E-14
3	CL -1	3.886E-05	4.411	3.733E-05	4.428	3.886E-05	4.411	-2.896E-18
6	I -1	7.753E-09	8.111	7.449E-09	8.128	7.753E-09	8.111	-1.623E-23
12	SIO3 -2	3.585E-12	11.446	3.052E-12	11.515	3.886E-05	4.411	-1.201E-17
57	NO3 -1	1.945E-05	4.711	1.868E-05	4.729	1.947E-05	4.711	-2.164E-16
59	CRO4 -2	9.456E-13	12.024	8.050E-13	12.094	9.760E-13	12.011	2.030E-27

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08

FIGURE B4. UNDEQ--CHARGE ADJUSTMENT BY VARYING SINGLE ION

FIGURE B4A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH CL- ADJUSTED FOR CHARGE
1   7  8  1  0  1  3 -1
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
```

FIGURE B4B.

CASE NUMBER 1


```
CASE PROGRESS
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  18 ITERATIONS.
SOLID  FE +3    OH -1      2 0-6  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  19 ITERATIONS.
SOLID  ZN +2    SIO3 -2   1 1 0  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  23 ITERATIONS.
IONIC STRENGTH CHANGED.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  27 ITERATIONS.
CHARGE ON THE SOLUTION ADJUSTED.
SOLUTIONS FOR CONSERVATICN OF MASS CONVERGE AT  29 ITERATIONS.
IONIC STRENGTH CHANGED.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  31 ITERATIONS.

  CHARGE ON SOLUTION (MOLES/LITER) =  3.628E-09

TOTAL CONCENTRATION OF CL - ADJUSTED TO  1.747E-05
ADJUSTED BY FACTOR OF  2.279
```

FIGURE B4C.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.318E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.859E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
-LOG KW = 13.965
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.817E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.654E-04	3.576	3.162E-04	3.500	2.052E-14
2	MG +2	9.883E-05	4.005	8.417E-05	4.075	1.000E-04	4.000	3.993E-15
5	NA +1	5.811E-05	4.300	4.815E-05	4.317	5.012E-05	4.300	1.066E-19
6	FE +3	1.778E-26	25.750	1.238E-26	25.907	5.012E-08	7.300	[illegible]
12	ZN +2	1.187E-07	6.925	1.011E-07	6.995	1.585E-07	6.800	-1.622E-11
19	CR +3	2.387E-15	14.622	1.662E-15	14.779	3.981E-09	8.400	-3.243E-22
1	CO3 -2	3.612E-06	5.442	3.076E-06	5.512	7.943E-04	3.100	2.777E-14
2	SO4 -2	2.987E-05	4.525	2.544E-05	4.594	3.162E-05	4.500	1.472E-15
3	CL -1	1.747E-05	4.758	1.678E-05	4.775	1.747E-05	4.758	1.974E-20
6	I -1	7.943E-09	8.100	7.632E-09	8.117	7.943E-09	8.100	1.543E-23
12	SIO3 -2	3.678E-12	11.435	3.125E-12	11.505	3.981E-05	4.400	[illegible]
57	NO3 -1	1.993E-05	4.701	1.915E-05	4.718	1.995E-05	4.700	3.276E-19
59	CRO4 -2	9.688E-13	12.014	8.250E-13	12.084	1.000E-12	12.000	-3.909E-28

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	3.897E-09

FIGURE B5. UNDEQ--CALCULATED PH

FIGURE B5A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH CALCULATED PH
1   7  8  1  1  1
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  5111  3111
4  2  6511  4511
4  3  6411  4411
4  6 10111  8111
4 12  6411  4411
4 57  6711  4711
4 59 14011 12011
```

FIGURE B5B.

CASE NUMBER 1 CASE 1

```
CASE PROGRESS
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  21 ITERATIONS.
SOLID  FE +3    OH -1     2 8-6  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  22 ITERATIONS.
SOLID  ZN +2    SIOJ -2   1 1 0  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  26 ITERATIONS.
IONIC STRENGTH CHANGED.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  30 ITERATIONS.
```

FIGURE 85C.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.318E-03

FIXED TOTAL HYDROGEN LESS HYDROXIDE = 8.634E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.636E-04
COMPUTED PH = 7.955 POH = 6.045
-LOG KW = 13.965
H+ ION CONCENTRATION = 7.938 OH- ION CONCENTRATION = 6.028
CARBONATE ALKALINITY = 7.624E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.117E-04	3.506	2.655E-04	3.576	3.162E-04	3.500	-2.616E-11
2	MG +2	9.886E-05	4.005	8.421E-05	4.075	1.000E-04	4.000	-7.624E-12
5	NA +1	5.011E-05	4.300	4.815E-05	4.317	5.012E-05	4.300	3.697E-16
6	FE +3	1.934E-26	25.713	1.348E-26	25.870	5.012E-08	7.300	0
12	ZN +2	1.190E-07	6.925	1.014E-07	6.994	1.581E-07	6.801	-4.198E-10
19	CR +3	2.323E-15	14.634	1.619E-15	14.791	3.981E-09	8.400	-9.269E-14
1	CO3 -2	3.564E-06	5.448	3.036E-06	5.518	7.745E-04	3.111	-1.012E-08
2	SO4 -2	2.913E-05	4.536	2.481E-05	4.605	3.083E-05	4.511	-2.395E-17
3	CL -1	3.881E-05	4.411	3.730E-05	4.428	3.882E-05	4.411	-7.253E-20
6	I -1	7.745E-09	8.111	7.442E-09	8.128	7.745E-09	8.111	-1.662E-23
12	SIO3 -2	3.663E-12	11.436	3.120E-12	11.506	3.882E-05	4.411	0
57	NO3 -1	1.943E-05	4.712	1.867E-05	4.729	1.945E-05	4.711	-4.862E-20
59	CRO4 -2	9.449E-13	12.025	8.049E-13	12.094	9.750E-13	12.011	-1.208E-20
	HYDROGEN	1.154E-08	7.938	1.169E-08	7.955	8.634E-04		-1.250E-08

SOLID						MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6		2.506E-08
ZN +2	SIO3 -2	1	1	0		2.248E-09

FIGURE B6. UMDEQ--FIXED CO2 ALKALINITY

FIGURE B6A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH FIXED CO3 ALKALINITY
1   7  8  1  0  0  0  0  1
2      1.2E-03
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  5104  3104
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
```

FIGURE 86B.

UNCORRECTED THERMODYNAMIC DATA FOR VERIFICATION

CASE 0

SOLIDS

METAL	LIGAND	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
1 CA +2																									
	1 CO3 -2	8.37	1	1	0	8.31	1	1	0																
	2 SO4 -2	4.64	1	1	0	4.85	1	1	0																
	12 SIO3 -2	7.20	1	1	0																				
	99 OH -1	-22.81	1	0	-2																				
2 MG +2																									
	1 CO3 -2	7.46	1	1	0	4.67	1	1	0	4.54	1	1	0	-10.01	2	1	-2	8.77	5	4	-2				
	12 SIO3 -2	10.29	1	1	0	-6.68	2	1	-2	11.06	3	2	-2	63.43	3	4	2	48.95	2	3	2	46.08	2	3	2
	99 OH -1	-16.84	1	0	-2																				
5 NA +1																									
	1 CO3 -2	1.31	2	1	0	-.13	2	1	0	10.88	1	1	1	11.12	3	2	1								
	2 SO4 -2	.18	2	1	0	1.11	2	1	0																
	3 CL -1	-1.58	1	1	0																				
	12 SIO3 -2	165.64	1	7	13																				
6 FE +3																									
	99 OH -1	-3.20	1	0	-3	-.80	1	0	-3	4.01	2	0	-6	-6.39	2	6	-6								
12 ZN +2																									
	1 CO3 -2	10.00	1	1	0																				
	3 CL -1	-15.20	2	1	-3																				
	12 SIO3 -2	18.50	1	1	0																				
	99 OH -1	-12.50	1	0	-2	-11.33	1	0	-2	-11.75	1	0	-2	-11.79	1	0	-2	-11.73	1	0	-2	-11.84	1	0	-2
		-11.53	1	0	-2																				
19 CR +3																									
	99 OH -1	-11.00	1	0	-3																				
50 H +1																									
	12 SIO3 -2	25.74	0	1	2	26.48	0	1	2	26.55	0	1	2	26.97	0	1	2								

COMPLEXES

METAL	LIGAND	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
1 CA +2																									
	1 CO3 -2	3.15	1	1	0	11.33	1	1	1																
	2 SO4 -2	2.31	1	1	0																				
	12 SIO3 -2	3.09	1	1	0	13.50	1	1	1	29.10	1	2	2												
	57 NO3 -1	.70	1	1	0	.60	1	2	0																
	99 OH -1	-12.85	1	0	-1																				
2 MG +2																									
	1 CO3 -2	2.88	1	1	0	11.28	1	1	1																
	2 SO4 -2	2.23	1	1	0																				
	3 CL -1	-1.00	1	1	0																				
	12 SIO3 -2	4.17	1	1	0	13.70	1	1	1	30.00	1	2	2												
	99 OH -1	-11.44	1	0	-1	-39.71	4	0	-4																
5 NA +1																									
	1 CO3 -2	1.20	1	1	0																				
	2 SO4 -2	.70	1	1	0																				
	3 CL -1	-1.85	1	1	0																				

```
            57 NO3 -1       -.60  1  1   0
            99 OH -1      -14.18  1  0  -1
 6 FE +3
             2 SO4 -2       4.04  1  1   0     5.38  1  2   0
             3 CL -1        1.48  1  1   0     2.13  1  2   0     1.30  1  3   0
             6 I  -1        3.50  1  1   0     2.40  1  2   0
            12 SIO3 -2     22.66  1  1   1
            57 NO3 -1       1.00  1  1   0
            59 CRO4 -2      7.81  1  1   0
            99 OH -1       -2.19  1  0  -1    -5.67  1  0  -2   -21.60  1  0  -4    -2.95  2  4  -2    -6.30  3  0  -4
12 ZN +2
             1 CO3 -2       4.70  1  1   0
             2 SO4 -2       2.38  1  1   0     3.20  1  2   0     1.70  1  3   0     1.70  1  4   0
             3 CL -1         .43  1  1   0      .61  1  2   0      .50  1  3   0      .20  1  4   0
             6 I  -1       -1.50  1  1   0    -1.76  1  2   0    -1.83  1  3   0    -2.42  1  4   0
            57 NO3 -1        .40  1  1   0     -.30  1  2   0
            99 OH -1       -8.96  1  0  -1   -28.40  1  0  -3   -41.20  1  0  -4   -16.90  1  0  -2    -9.00  2  0  -1
19 CR +3
             2 SO4 -2       2.70  1  1   0
             3 CL -1         .80  1  1   0      .01  1  2   0
            99 OH -1       -4.00  1  0  -1    -9.70  1  0  -2   -27.40  1  0  -4    -5.06  2  0  -2    -8.15  3  0  -4   -18.00  1  0  -3
50 H  +1
             1 CO3 -2      10.33  0  1   1    16.68  0  1   2
             2 SO4 -2       1.99  0  1   1
            12 SIO3 -2     13.10  0  1   1    23.00  0  1   2    55.90  0  4   4    78.20  0  4   6
            59 CRO4 -2      6.51  0  1   1    14.55  0  2   2     6.31  0  1   2

MIXED COMPLEXES
---------------
MET    LIG    ION3      LOG K M  L I3  H   LOG K M  L I3  H   LOG K M  L I3  H   LOG K M  L I3  H   LOG K M  L I3  H
---    ---    ----      ----------------   ----------------   ----------------   ----------------   ----------------
ZN +2  CL -1  I  -1      .99  1  2  1  0    .69  1  1  2  0   1.51  1  3  1  0   1.11  1  2  2  0
```

FIGURE D6C.

USER INPUT DATA

CASE 0

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 45 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-03

THE CONDITIONS FOR THE 1 CASES ARE

	NUMBER	TOTAL CONCENTRATIONS CASE 1
-LOG(MOLES/L)		
METALS		
CA +2	1	3.500
MG +2	2	4.000
NA +1	5	4.300
FE +3	6	7.300
ZN +2	12	6.800
CR +3	19	8.400
LIGANDS		
CO3 -2	1	3.104
SO4 -2	2	4.500
CL -1	3	4.400
I -1	6	8.100
SIO3 -2	12	4.400
NO3 -1	57	4.700
CRO4 -2	59	12.000

FIXED PH 7.950
CO3 CONCENTRATIONS SHOWN ARE CARBONATE ALKALINITY.

FIGURE 86D.

CASE 1

FINAL ION AND SOLID CONCENTRATIONS

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.915E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.917E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.870E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	1.082E-16
2	MG +2	9.882E-05	4.005	8.474E-05	4.072	1.000E-04	4.000	5.610E-17
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	8.388E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-09	7.300	0
12	ZN +2	1.180E-07	6.928	1.012E-07	6.995	1.585E-07	6.800	-1.410E-11
19	CR +3	2.354E-15	14.628	1.665E-15	14.779	3.981E-09	8.400	1.985E-22
1	CO3 -2	3.619E-06	5.441	3.103E-06	5.508	7.998E-04	3.097	1.277E-05
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	-1.740E-19
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-7.356E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	-2.358E-23
12	SIO3 -2	3.646E-12	11.438	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.993E-05	4.701	1.918E-05	4.717	1.995E-05	4.700	-3.085E-20
59	CRO4 -2	9.687E-13	12.014	8.307E-13	12.081	1.000E-12	12.000	-1.249E-27

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	3.768E-09

FIGURE B7. UNDEQ--CO2 PRESSURE VARIABLE

FIGURE B7A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH CO2 PRESENT
1    7  8  5  0  0  0  0  2
2       1.2E-03
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795   400   795   895
6     0     35
```

FIGURE 87B.

USER INPUT DATA

CASE 0

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 46 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-03

THE CONDITIONS FOR THE 5 CASES ARE

-LOG(MOLES/L)	NUMBER	TOTAL CONCENTRATIONS CASE 1	CASE 2	CASE 3	CASE 4	CASE 5
METALS						
CA +2	1	3.500	3.500	3.500	3.500	3.500
MG +2	2	4.000	4.000	4.000	4.000	4.000
NA +1	5	4.300	4.300	4.300	4.300	4.300
FE +3	6	7.300	7.300	7.300	7.300	7.300
ZN +2	12	6.800	6.800	6.800	6.800	6.800
CR +3	19	8.400	8.400	8.400	8.400	8.400
LIGANDS						
CO3 -2	1	3.100	3.100	3.100	3.100	.100
SO4 -2	2	4.500	4.500	4.500	4.500	4.500
CL -1	3	4.400	4.400	4.400	4.400	4.400
I -1	6	8.100	8.100	8.100	8.100	8.100
SIO3 -2	12	4.400	4.400	4.400	4.400	4.400
NO3 -1	57	4.700	4.700	4.700	4.700	4.700
CRO4 -2	59	12.000	12.000	12.000	12.000	12.000
FIXED PH		7.950	4.000	7.950	8.950	8.950
-LOG CO2 IN ATM		0	3.500	3.500	3.500	3.500

FIGURE 87C.

CASE 1

FINAL ION AND SOLID CONCENTRATIONS

FINAL IONIC STRENGTH = 1.208E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.859E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.816E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	1.232E-16
2	MG +2	9.882E-05	4.005	8.475E-05	4.072	1.000E-04	4.000	6.330E-17
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-3.389E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.180E-07	6.928	1.012E-07	6.995	1.585E-07	6.800	-1.582E-11
19	CR +3	2.354E-15	14.628	1.665E-15	14.779	3.981E-09	8.400	1.191E-22
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	4.337E-17
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	-2.050E-19
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-6.422E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	-8.936E-24
12	SIO3 -2	3.646E-12	11.438	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.993E-05	4.701	1.918E-05	4.717	1.995E-05	4.700	5.075E-20
59	CRO4 -2	9.687E-13	12.014	8.307E-13	12.081	1.000E-12	12.000	-1.249E-27

SOLID						MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6		2.506E-08
ZN +2	SIO3 -2	1	1	0		3.874E-09

FIGURE B7D.

FINAL ION AND SOLID CONCENTRATIONS

CASE 2

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 4.000 POH = 10.000
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 1.772E-03 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 2.057E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 3.983 OH- ION CONCENTRATION = 9.983
CARBONATE ALKALINITY = -1.038E-04
LOG FORMATION CONSTANT FOR CO2 = 18.04

-LOG PARTIAL PRESSURE OF PCO2 = 3.50

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.148E-04	3.502	2.700E-04	3.569	3.162E-04	3.500	-1.000E-13
2	MG +2	9.963E-05	4.002	8.544E-05	4.068	1.000E-04	4.000	-2.392E-14
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-1.452E-17
6	FE +3	1.397E-14	13.855	9.886E-15	14.005	5.012E-08	7.300	0
12	ZN +2	1.576E-07	6.802	1.352E-07	6.869	1.585E-07	6.800	2.955E-12
19	CR +3	2.153E-09	8.667	1.523E-09	8.817	3.981E-09	8.400	-1.705E-18
1	CO3 -2	2.671E-14	13.573	2.291E-14	13.640	7.943E-04	3.100	0
2	SO4 -2	2.959E-05	4.529	2.538E-05	4.596	3.162E-05	4.500	2.824E-12
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-3.821E-18
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	3.510E-24
12	SIO3 -2	4.644E-20	19.333	3.982E-20	19.400	3.981E-05	4.400	1.859E-23
57	NO3 -1	1.993E-05	4.701	1.918E-05	4.717	1.995E-05	4.700	-1.357E-18
59	CRO4 -2	3.456E-15	14.461	2.964E-15	14.528	1.000E-12	12.000	-2.169E-26

SOLID						MOLES PER LITER OF SOLUTION
H +1	CO3 -2	0	1	2		7.833E-04
FE +3	OH -1	2	0	-6		2.586E-08

FIGURE B7E.

FINAL ION AND SOLID CONCENTRATIONS

CASE 3

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 1.206E-03 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 5.552E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 4.619E-04
LOG FORMATION CONSTANT FOR CO2 = 18.04

-LOG PARTIAL PRESSURE OF PCO2 = 3.50

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.129E-04	3.505	2.603E-04	3.571	3.162E-04	3.500	7.075E-15
2	MG +2	9.914E-05	4.004	8.502E-05	4.070	1.000E-04	4.000	3.636E-15
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	1.303E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.100E-07	6.920	1.012E-07	6.995	1.576E-07	6.802	-9.074E-10
19	CR +3	2.354E-15	14.620	1.665E-15	14.779	3.981E-09	8.400	-1.985E-23
1	CO3 -2	2.122E-06	5.673	1.820E-06	5.740	7.943E-04	3.100	0
2	SO4 -2	2.904E-05	4.525	2.559E-05	4.592	3.162E-05	4.500	-5.073E-19
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-3.957E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	5.445E-25
12	SIO3 -2	3.645E-12	11.430	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.993E-05	4.701	1.918E-05	4.717	1.995E-05	4.700	4.533E-20
59	CRO4 -2	9.687E-13	12.014	8.307E-13	12.081	1.000E-12	12.000	-1.249E-27

SOLID						MOLES PER LITER OF SOLUTION
H +1	CO3 -2	0	1	2		3.253E-04
FE +3	OH -1	2	0	-6		2.506E-08
ZN +2	SIO3 -2	1	1	0		9.360E-09

FIGURE B7F.

CASE NUMBER 4


```
CASE PROGRESS
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT   5 ITERATIONS.
SOLID  H  +1    CO3 -2    0 1 2  DISSOLVES.

CO2 JUST DISSOLVED.  THE TOTAL CO3 WAS NOT SUFFICIENT TO SATURATE THE SOLUTION WITH CO2 AT THIS PH.
THIS SOLUTION IS NO LONGER AT EQUILIBRIUM WITH ANY CO2 IN THE ATMOSPHERE. UNLESS H2CO3 PRECIPITATES BELOW.

SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT   8 ITERATIONS.
SOLID  CA +2    CO3 -2    1 1 0  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  13 ITERATIONS.

  CHARGE ON SOLUTION (MOLES/LITER) = -1.988E-04

   THE SOLUTION CHARGE IMBALANCE EXCEEDS 0.1 PERCENT* OF THE IONIC STRENGTH.
DO NOT USE THESE RESULTS FOR INPUT TO OTHER COMPUTER RUNS.
```

FIGURE B7G.

FINAL ION AND SOLID CONCENTRATIONS

CASE 4

FINAL IONIC STRENGTH = 1.288E-03

FIXED PH = 8.950 POH = 5.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 7.894E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 7.896E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 8.933 OH- ION CONCENTRATION = 5.035
CARBONATE ALKALINITY = 7.253E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	1.939E-04	3.712	1.663E-04	3.779	3.162E-04	3.500	-2.523E-10
2	MG +2	9.725E-05	4.012	8.340E-05	4.079	1.000E-04	4.000	7.911E-13
5	NA +1	5.009E-05	4.300	4.821E-05	4.317	5.012E-05	4.300	7.635E-15
6	FE +3	1.974E-29	28.705	1.396E-29	28.855	5.012E-08	7.300	0
12	ZN +2	1.307E-09	8.884	1.120E-09	8.951	1.585E-07	6.800	5.370E-16
19	CR +3	4.965E-18	17.304	3.512E-18	17.454	3.981E-09	8.400	7.014E-22
1	CO3 -2	2.991E-05	4.524	2.565E-05	4.591	7.943E-04	3.100	0
2	SO4 -2	3.836E-05	4.518	2.604E-05	4.584	3.162E-05	4.500	-8.895E-15
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	3.462E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	2.277E-23
12	SIO3 -2	3.291E-10	9.483	2.822E-10	9.549	3.981E-05	4.400	0
57	NO3 -1	1.994E-05	4.700	1.919E-05	4.717	1.995E-05	4.700	-5.212E-18
59	CRO4 -2	9.968E-13	12.001	8.540E-13	12.068	1.000E-12	12.000	1.803E-27

SOLID					MOLES PER LITER OF SOLUTION
CA +2	CO3 -2	1	1	0	1.143E-04
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	1.434E-07

FIGURE D7H.

FINAL ION AND SOLID CONCENTRATIONS

CASE 5

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 8.950 POH = 5.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 1.503E+00 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 4.627E-03
-LOG KW = 13.967
H+ ION CONCENTRATION = 8.933 OH- ION CONCENTRATION = 5.033
CARBONATE ALKALINITY = 5.086E-03
LOG FORMATION CONSTANT FOR CO2 = 18.04

-LOG PARTIAL PRESSURE OF PCO2 = 3.50

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	2.734E-05	4.563	2.344E-05	4.630	3.162E-04	3.500	0
2	MG +2	8.622E-05	4.064	7.394E-05	4.131	1.000E-04	4.000	-1.085E-09
5	NA +1	4.997E-05	4.301	4.009E-05	4.318	5.012E-05	4.300	-4.201E-13
6	FE +3	1.974E-29	28.705	1.396E-29	28.855	5.012E-08	7.300	0
12	ZN +2	1.306E-09	8.884	1.120E-09	8.951	1.585E-07	6.800	-2.731E-12
19	CR +3	4.965E-18	17.304	3.512E-18	17.454	3.981E-09	8.400	-1.456E-22
1	CO3 -2	2.122E-04	3.673	1.820E-04	3.740	7.943E-01	.100	0
2	SO4 -2	3.115E-05	4.507	2.671E-05	4.573	3.162E-05	4.500	-1.086E-09
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-3.563E-17
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	1.159E-24
12	SIO3 -2	3.292E-10	9.483	2.823E-10	9.549	3.981E-05	4.400	0
57	NO3 -1	1.995E-05	4.700	1.920E-05	4.717	1.995E-05	4.700	-4.113E-16
59	CRO4 -2	9.968E-13	12.001	8.548E-13	12.068	1.000E-12	12.000	1.803E-27

SOLID					MOLES PER LITER OF SOLUTION
H +1	CO3 -2	0	1	2	7.893E-01
CA +2	CO3 -2	1	1	0	2.817E-04
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	1.346E-07

FIGURE B8. UMDEQ--FIXED REDOX POTENTIAL

FIGURE B8A. INPUT CARDS

```
 0  SHORT LAKE SUPERIOR DATA WITH FIXED REDOX POTENTIAL
 1   7  8  5  0  0  0  0  0  1
 2     1.2E-03
 3  1  55    35
 3  2  60    40
 3  5  63    43
 3  6  93    73
 3 12  88    68
 3 19 104    84
 4  1  51    31
 4  2  65    45
 4  3  64    44
 4  6 101    81
 4 12  64    44
 4 57  67    47
 4 59 140   120
 5     795
 7    120    80    40    00   -40
10 16 13
```

FIGURE B8B.

USER INPUT DATA

CASE 0

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 46 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-30

THE CONDITIONS FOR THE 5 CASES ARE

-LOG(MOLES/L)	NUMBER	TOTAL CONCENTRATIONS CASE 1	CASE 2	CASE 3	CASE 4	CASE 5
METALS						
CA +2	1	3.500	3.500	3.500	3.500	3.500
MG +2	2	4.000	4.000	4.000	4.000	4.000
NA +1	5	4.300	4.300	4.300	4.300	4.300
FE +3	6	7.300	7.300	7.300	7.300	7.300
ZN +2	12	6.800	6.800	6.800	6.800	6.800
CR +3	19	8.400	8.400	8.400	8.400	8.400
LIGANDS						
CO3 -2	1	3.100	3.100	3.100	3.100	3.100
SO4 -2	2	4.500	4.500	4.500	4.500	4.500
CL -1	3	4.400	4.400	4.400	4.400	4.400
I -1	6	8.100	8.100	8.100	8.100	8.100
SIO3 -2	12	4.400	4.400	4.400	4.400	4.400
NO3 -1	57	4.700	4.700	4.700	4.700	4.700
CRO4 -2	59	12.000	12.000	12.000	12.000	12.000
FIXED PH		7.950	7.950	7.950	7.950	7.950
REDOX POTENTIAL		12.000	8.000	4.000	0	-4.000

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

FE3O4 CR3/CRO4

FIGURE 88C.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.200E-30

FIXED PH = 7.950
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.868E-04 POH = 6.050
-LOG KW = 14.000 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
H+ ION CONCENTRATION = 7.950
CARBONATE ALKALINITY = 7.808E-04 OH- ION CONCENTRATION = 6.050

FIXED PE = 12.00

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.106E-04	3.508	3.106E-04	3.508	3.162E-04	3.500	7.478E-17
2	MG +2	9.856E-05	4.006	9.856E-05	4.006	1.000E-04	4.000	3.879E-17
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-05	4.300	6.555E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	-8.664E-12
19	CR +3	7.667E-34	33.115	7.667E-34	33.115	0	******	0
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	4.445E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	-1.533E-19
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-1.547E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-1.310E-23
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	4.711E-21
59	CRO4 -2	3.843E-09	8.415	3.843E-09	8.415	3.982E-09	8.400	0

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	2.036E-08

FIGURE 88D.

CASE 2

FINAL ION AND SOLID CONCENTRATIONS

FINAL IONIC STRENGTH = 1.200E-30

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.860E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
-LOG KW = 14.000
H+ ION CONCENTRATION = 7.950 OH- ION CONCENTRATION = 6.050
CARBONATE ALKALINITY = 7.800E-04

FIXED PE = 8.00

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.106E-04	3.508	3.106E-04	3.508	3.162E-04	3.500	7.478E-17
2	MG +2	9.856E-05	4.006	9.856E-05	4.006	1.000E-04	4.000	3.879E-17
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-05	4.300	6.555E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	-8.664E-12
19	CR +3	7.667E-22	21.115	7.667E-22	21.115	1.784E-15	14.749	1.784E-15
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	4.445E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	-1.532E-19
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-1.547E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-1.310E-23
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	4.711E-21
59	CRO4 -2	3.843E-09	8.415	3.843E-09	8.415	3.902E-09	8.400	1.784E-15

SOLID						MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6		2.506E-08
ZN +2	SIO3 -2	1	1	0		2.036E-08

FIGURE 88E.

FINAL ION AND SOLID CONCENTRATIONS

CASE 3

FINAL IONIC STRENGTH = 1.200E-30

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.868E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
-LOG KW = 14.000
H+ ION CONCENTRATION = 7.950 OH- ION CONCENTRATION = 6.050
CARBONATE ALKALINITY = 7.808E-04

FIXED PE = 4.00

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.106E-04	3.500	3.106E-04	3.500	3.162E-04	3.500	8.637E-19
2	MG +2	9.856E-05	4.006	9.856E-05	4.006	1.000E-04	4.000	-1.406E-19
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-05	4.300	1.283E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	1.116E-10
19	CR +3	1.711E-15	14.767	1.711E-15	14.767	3.982E-09	8.400	6.555E-10
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	3.166E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	-8.206E-20
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-5.197E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-7.590E-24
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	2.092E-20
59	CRO4 -2	8.577E-15	14.067	8.577E-15	14.067	8.888E-15	14.051	6.555E-10

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	2.036E-08

FIGURE B8F.

FINAL ION AND SOLID CONCENTRATIONS

CASE 4

FINAL IONIC STRENGTH = 1.200E-30

FIXED PH = 7.950
POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.868E-04
SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
-LOG KW = 14.000
H+ ION CONCENTRATION = 7.950
OH- ION CONCENTRATION = 6.050
CARBONATE ALKALINITY = 7.808E-04

FIXED PE = 0

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.106E-04	3.508	3.106E-04	3.508	3.162E-04	3.500	3.758E-19
2	MG +2	9.856E-05	4.006	9.856E-05	4.006	1.000E-04	4.000	-2.694E-19
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-05	4.300	1.246E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	1.114E-18
19	CR +3	1.711E-15	14.767	1.711E-15	14.767	3.982E-09	8.400	2.249E-16
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	-7.405E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	1.348E-19
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-5.197E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-7.590E-24
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	2.092E-20
59	CRO4 -2	8.577E-27	26.067	8.577E-27	26.067	6.462E-27	26.190	2.249E-16

SOLID						MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6		2.506E-08
ZN +2	SIO3 -2	1	1	0		2.036E-08

FIGURE 88G.

FINAL ION AND SOLID CONCENTRATIONS

CASE 5

FINAL IONIC STRENGTH = 1.200E-30

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.860E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
-LOG KW = 14.000
H+ ION CONCENTRATION = 7.950 OH- ION CONCENTRATION = 6.050
CARBONATE ALKALINITY = 7.808E-04

FIXED PE = -4.00

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.106E-04	3.508	3.106E-04	3.508	3.162E-04	3.500	3.750E-19
2	MG +2	9.856E-05	4.006	9.856E-05	4.006	1.000E-04	4.000	-2.694E-19
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-05	4.300	1.246E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	1.114E-18
19	CR +3	1.711E-15	14.767	1.711E-15	14.767	3.982E-09	8.400	2.249E-16
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	-7.405E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	1.348E-19
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-5.197E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-7.590E-24
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	2.092E-20
59	CRO4 -2	8.577E-39	38.067	8.577E-39	38.067	0	******	2.249E-16

SOLID						MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6		2.506E-08
ZN +2	SIO3 -2	1	1	0		2.036E-08

FIGURE B9. UNDEQ--FIXED REDOX POTENTIAL

FIGURE B9A. INPUT DATA

```
0  SHORT LAKE SUPERIOR DATA WITH FIXED REDOX POTENTIAL (EH)
1   7  8  5  0  0  0  0  0  1
2     1.2E-03
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
7  1   710   473   237  00    -237
```

FIGURE B9B.

USER INPUT DATA

CASE 0

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 46 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-30

THE CONDITIONS FOR THE 5 CASES ARE

-LOG(MOLES/L)	NUMBER	TOTAL CONCENTRATIONS CASE 1	CASE 2	CASE 3	CASE 4	CASE 5
METALS						
CA +2	1	3.500	3.500	3.500	3.500	3.500
MG +2	2	4.000	4.000	4.000	4.000	4.000
NA +1	5	4.300	4.300	4.300	4.300	4.300
FE +3	6	7.300	7.300	7.300	7.300	7.300
ZN +2	12	6.800	6.800	6.800	6.800	6.800
CR +3	19	8.400	8.400	8.400	8.400	8.400
LIGANDS						
CO3 -2	1	3.100	3.100	3.100	3.100	3.100
SO4 -2	2	4.500	4.500	4.500	4.500	4.500
CL -1	3	4.400	4.400	4.400	4.400	4.400
I -1	6	8.100	8.100	8.100	8.100	8.100
SIO3 -2	12	4.400	4.400	4.400	4.400	4.400
NO3 -1	57	4.700	4.700	4.700	4.700	4.700
CRO4 -2	59	12.000	12.000	12.000	12.000	12.000
FIXED PH		7.950	7.950	7.950	7.950	7.950
REDOX POTENTIAL		12.002	7.996	4.006	0	-4.006

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

FE3O4 CR3/CRO4

FIGURE 89C.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.208E-30

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.868E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
-LOG KW = 14.000
H+ ION CONCENTRATION = 7.950 OH- ION CONCENTRATION = 6.050
CARBONATE ALKALINITY = 7.808E-04

FIXED PE = 12.00

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.106E-04	3.508	3.106E-04	3.508	3.162E-04	3.500	7.478E-17
2	MG +2	9.856E-05	4.006	9.856E-05	4.006	1.000E-04	4.000	3.879E-17
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-05	4.300	6.555E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	-8.664E-12
19	CR +3	7.570E-34	33.121	7.570E-34	33.121	0	******	0
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	4.445E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	-1.533E-19
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-1.547E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-1.310E-23
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	4.711E-21
59	CRO4 -2	3.843E-09	8.415	3.843E-09	8.415	3.982E-09	8.400	0

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	2.036E-08

FIGURE B9D.

CASE 2

FINAL ION AND SOLID CONCENTRATIONS

FINAL IONIC STRENGTH = 1.200E-30

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.668E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
-LOG KW = 14.000
H+ ION CONCENTRATION = 7.950 OH- ION CONCENTRATION = 6.050
CARBONATE ALKALINITY = 7.600E-04

FIXED PE = 8.00

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.166E-04	3.500	3.106E-04	3.500	3.162E-04	3.500	7.470E-17
2	MG +2	9.856E-05	4.006	9.856E-05	4.006	1.000E-04	4.000	3.879E-17
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-65	4.300	6.555E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-00	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	-8.664E-12
19	CR +3	7.904E-22	21.102	7.904E-22	21.102	1.839E-15	14.735	1.839E-15
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	4.445E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	-1.532E-19
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-1.547E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-1.310E-23
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	4.711E-21
59	CRO4 -2	3.843E-09	8.415	3.843E-09	8.415	3.982E-09	8.400	1.839E-15

SOLID						MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6		2.506E-00
ZN +2	SIO3 -2	1	1	0		2.036E-00

FIGURE 89E.

FINAL ION AND SOLID CONCENTRATIONS

CASE 3

FINAL IONIC STRENGTH = 1.200E-30

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.860E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
-LOG KW = 14.000
H+ ION CONCENTRATION = 7.950 OH- ION CONCENTRATION = 6.050
CARBONATE ALKALINITY = 7.800E-04

FIXED PE = 4.01

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.106E-04	3.500	3.106E-04	3.500	3.162E-04	3.500	8.637E-19
2	MG +2	9.856E-05	4.006	9.856E-05	4.006	1.000E-04	4.000	-1.406E-19
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-05	4.300	1.283E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	1.122E-18
19	CR +3	1.711E-15	14.767	1.711E-15	14.767	3.982E-09	8.400	1.436E-18
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	3.166E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	-8.206E-20
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-5.197E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-7.590E-24
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	2.092E-20
59	CRO4 -2	8.955E-15	14.048	8.955E-15	14.048	9.280E-15	14.032	1.436E-18

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	2.036E-08

FIGURE 89F.

FINAL ION AND SOLID CONCENTRATIONS

CASE 4

FINAL IONIC STRENGTH = 1.200E-30

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.860E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
-LOG KW = 14.000
H+ ION CONCENTRATION = 7.950 OH- ION CONCENTRATION = 6.050
CARBONATE ALKALINITY = 7.000E-04

FIXED PE = 0

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.106E-04	3.508	3.106E-04	3.508	3.162E-04	3.500	3.750E-19
2	MG +2	9.056E-05	4.006	9.056E-05	4.006	1.000E-04	4.000	-2.694E-19
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-05	4.300	1.246E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	1.120E-18
19	CR +3	1.711E-15	14.767	1.711E-15	14.767	3.982E-09	8.400	2.249E-16
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	-7.405E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	1.348E-19
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-5.197E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-7.590E-24
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	2.092E-20
59	CRO4 -2	8.577E-27	26.067	8.577E-27	26.067	6.462E-27	26.190	2.249E-16

SOLID						MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6		2.506E-08
ZN +2	SIO3 -2	1	1	0		2.036E-08

FIGURE B9G.

FINAL ION AND SOLID CONCENTRATIONS

CASE 5

FINAL IONIC STRENGTH = 1.200E-30

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.868E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
-LOG KW = 14.000
H+ ION CONCENTRATION = 7.950 OH- ION CONCENTRATION = 6.050
CARBONATE ALKALINITY = 7.808E-04

FIXED PE = -4.01

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.106E-04	3.508	3.106E-04	3.508	3.162E-04	3.500	3.758E-19
2	MG +2	9.856E-05	4.006	9.856E-05	4.006	1.000E-04	4.000	-2.694E-19
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-05	4.300	1.246E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	1.120E-18
19	CR +3	1.711E-15	14.767	1.711E-15	14.767	3.982E-09	8.400	2.249E-16
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	-7.405E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	1.340E-19
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-5.197E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-7.590E-24
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	2.092E-20
59	CRO4 -2	8.215E-39	38.085	8.215E-39	38.085	0	******	2.249E-16

SOLID						MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	8	-6		2.586E-08
ZN +2	SIO3 -2	1	1	0		2.036E-08

FIGURE B10. UNDEQ--FIXED REDOX POTENTIAL(O2)

FIGURE B10A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH FIXED REDOX POTENTIAL (O2)
1   7  8  4  0  0  0  0  0  1
2     1.2E-03
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
7  2 100    60    10    0001
```

FIGURE B10B.

USER INPUT DATA

CASE 8

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 46 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-30

THE CONDITIONS FOR THE 4 CASES ARE

	NUMBER	TOTAL CONCENTRATIONS CASE 1	CASE 2	CASE 3	CASE 4
-LOG(MOLES/L)					
METALS					
CA +2	1	3.500	3.500	3.500	3.500
MG +2	2	4.000	4.000	4.000	4.000
NA +1	5	4.300	4.300	4.300	4.300
FE +3	6	7.300	7.300	7.300	7.300
ZN +2	12	6.800	6.800	6.800	6.800
CR +3	19	8.400	8.400	8.400	8.400
LIGANDS					
CO3 -2	1	3.100	3.100	3.100	3.100
SO4 -2	2	4.500	4.500	4.500	4.500
CL -1	3	4.400	4.400	4.400	4.400
I -1	6	8.100	8.100	8.100	8.100
SIO3 -2	12	4.400	4.400	4.400	4.400
NO3 -1	57	4.700	4.700	4.700	4.700
CRO4 -2	59	12.000	12.000	12.000	12.000
FIXED PH		7.950	7.950	7.950	7.950
REDOX POTENTIAL		2.562	2.507	2.312	1.562

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

FE3O4 CR3/CRO4

FIGURE B10C.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.280E-30

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.868E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.869E-04
-LOG KW = 14.000
H+ ION CONCENTRATION = 7.950 OH- ION CONCENTRATION = 6.050
CARBONATE ALKALINITY = 7.808E-04

FIXED PE = 2.56

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.106E-04	3.508	3.106E-04	3.508	3.162E-04	3.500	7.506E-17
2	MG +2	9.856E-05	4.006	9.856E-05	4.006	1.000E-04	4.000	3.884E-17
5	NA +1	5.011E-05	4.300	5.011E-05	4.300	5.012E-05	4.300	5.977E-20
6	FE +3	1.396E-26	25.855	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.012E-07	6.995	1.012E-07	6.995	1.585E-07	6.800	-8.664E-12
19	CR +3	1.711E-15	14.767	1.711E-15	14.767	3.982E-09	8.400	1.343E-22
1	CO3 -2	3.198E-06	5.495	3.198E-06	5.495	7.943E-04	3.100	4.445E-17
2	SO4 -2	2.927E-05	4.534	2.927E-05	4.534	3.162E-05	4.500	-9.049E-20
3	CL -1	3.981E-05	4.400	3.981E-05	4.400	3.981E-05	4.400	-1.928E-20
6	I -1	7.943E-09	8.100	7.943E-09	8.100	7.943E-09	8.100	-1.310E-23
12	SIO3 -2	3.126E-12	11.505	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.992E-05	4.701	1.995E-05	4.700	4.711E-21
59	CRO4 -2	4.162E-19	18.381	4.162E-19	18.381	4.313E-19	18.365	1.343E-22

SOLID						MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	8	-6		2.506E-08
ZN +2	SIO3 -2	1	1	0		2.036E-08

FIGURE B11. UNDEQ--VARIABLE REDOX POTENTIAL(PE CALCULATED)

FIGURE B11A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH REDOX WITH CAP. AND INT.
1   7  8  1  1  1  0  0  0  2  0  0  0  0  3
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 16802 14802
4  1  5111  3111
4  2  6511  4511
4  3  6411  4411
4  6 10111  8111
4 12  6411  4411
4 57  6711  4711
4 59 10411  8411
7    100
8    167-08
```

FIGURE B11B.

USER INPUT DATA

CASE 8

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 46 POSSIBLE SOLIDS.

IONIC STRENGTH WILL BE CALCULATED.

THE CONDITIONS FOR THE 1 CASES ARE

	NUMBER	TOTAL CONCENTRATIONS CASE 1
-LOG(MOLES/L)		
METALS		
CA +2	1	3.500
MG +2	2	4.000
NA +1	5	4.300
FE +3	6	7.300
ZN +2	12	6.800
CR +3	19	14.802
LIGANDS		
CO3 -2	1	3.111
SO4 -2	2	4.511
CL -1	3	4.411
I -1	6	8.111
SIO3 -2	12	4.411
NO3 -1	57	4.711
CRO4 -2	59	8.411
REDOX POTENTIAL		18.000
E- CONCENTRATION		1.670E-08

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

FE3O4 CR3/CRO4

THE FOLLOWING 1 SOLIDS ARE ASSUMED 'PRESENT INITIALLY'

FE +3 OH -1 3 8 -8

FIGURE B11C.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.318E-03

FIXED TOTAL HYDROGEN LESS HYDROXIDE = 8.634E-04
COMPUTED PH = 7.955 POH = 6.045 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.636E-04
-LOG KH = 13.965
H+ ION CONCENTRATION = 7.938
CARBONATE ALKALINITY = 7.624E-04 OH- ION CONCENTRATION = 6.028

CALCULATED PE = -4.78

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.117E-04	3.506	2.655E-04	3.576	3.162E-04	3.500	-2.616E-11
2	MG +2	9.886E-05	4.005	8.421E-05	4.075	1.000E-04	4.000	-7.025E-12
5	NA +1	5.011E-05	4.300	4.815E-05	4.317	5.012E-05	4.300	3.695E-16
6	FE +3	1.935E-26	25.713	1.348E-26	25.870	5.012E-08	7.300	0
12	ZN +2	1.190E-07	6.925	1.014E-07	6.994	1.581E-07	6.801	-4.198E-10
19	CR +3	2.265E-15	14.645	1.578E-15	14.802	3.881E-09	8.411	-9.037E-14
1	CO3 -2	3.564E-06	5.448	3.036E-06	5.518	7.745E-04	3.111	-1.012E-08
2	SO4 -2	2.913E-05	4.536	2.481E-05	4.605	3.083E-05	4.511	-2.094E-17
3	CL -1	3.881E-05	4.411	3.730E-05	4.428	3.882E-05	4.411	-1.060E-21
6	I -1	7.745E-09	8.111	7.442E-09	8.128	7.745E-09	8.111	1.636E-23
12	SIO3 -2	3.663E-12	11.436	3.120E-12	11.506	3.882E-05	4.411	0
57	NO3 -1	1.943E-05	4.712	1.867E-05	4.729	1.945E-05	4.711	2.794E-20
59	CRO4 -2	8.095E-41	40.092	6.896E-41	40.161	0	******	-9.037E-14
	HYDROGEN	1.154E-08	7.938	1.109E-08	7.955	8.634E-04		-1.200E-08
	ELECTRONS	4.995E+04	-4.699			5.055E-09		-1.059E-22

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	1.748E-08
ZN +2	SIO3 -2	1	1	0	2.247E-09
FE +3	OH -1	3	0	-8	5.055E-09

FIGURE B11D.

INTERACTION CAPACITIES

CASE 1

	H +1	CA +2	MG +2	NA +1	FE +3	ZN +2	CR +3	CO3 -2	SO4 -2	CL -1	I -1	SIO3 -2
H +1	-1.77E+04	-6.71E+01	-4.18E+01	-8.79E-01	-5.32E+04	-3.52E+04	-4.11E+04	1.80E+04	4.11E+00	9.95E-03	1.13E-04	3.52E+04
CA +2	-6.71E+01	-1.37E+03	-4.12E-01	-1.10E-02	-2.01E+02	-1.33E+02	-1.55E+02	7.37E+01	5.99E+01	3.97E-05	4.26E-07	1.33E+02
MG +2	-4.18E+01	-4.12E-01	-4.34E+03	-8.49E-03	-1.25E+02	-8.28E+01	-9.68E+01	4.67E+01	5.00E+01	3.66E-02	2.66E-07	8.28E+01
NA +1	-8.79E-01	-1.10E-02	-8.49E-03	-8.66E+03	-2.64E+00	-1.74E+00	-2.04E+00	9.21E-01	1.75E+00	5.66E-03	5.50E-09	1.74E+00
FE +3	-5.32E+04	-2.01E+02	-1.25E+02	-2.64E+00	-1.60E+05	-1.06E+05	-1.23E+05	5.41E+04	1.23E+01	2.90E-02	3.30E-04	1.06E+05
ZN +2	-3.52E+04	-1.33E+02	-8.28E+01	-1.74E+00	-1.06E+05	-8.00E+04	-8.14E+04	3.58E+04	8.36E+00	2.28E-02	2.59E-04	8.00E+04
CR +3	-4.11E+04	-1.55E+02	-9.68E+01	-2.04E+00	-1.23E+05	-8.14E+04	-1.12E+00	4.18E+04	9.52E+00	2.30E-02	2.61E-04	8.14E+04
CO3 -2	1.80E+04	7.37E+01	4.67E+01	9.21E-01	5.41E+04	3.58E+04	4.18E+04	-1.89E+04	-4.47E+00	-1.01E-02	-1.15E-04	-3.58E+04
SO4 -2	4.11E+00	5.99E+01	5.00E+01	1.75E+00	1.23E+01	8.36E+00	9.52E+00	-4.47E+00	-1.41E+04	-4.24E-04	-2.60E-08	-8.36E+00
CL -1	9.95E-03	3.97E-05	3.66E-02	5.66E-03	2.90E-02	2.28E-02	2.30E-02	-1.01E-02	-4.24E-04	-1.12E+04	-4.21E-11	-2.28E-02
I -1	1.13E-04	4.26E-07	2.66E-07	5.50E-09	3.30E-04	2.59E-04	2.61E-04	-1.15E-04	-2.60E-08	-4.21E-11	-5.61E+07	-2.59E-04
SIO3 -2	3.52E+04	1.33E+02	8.28E+01	1.74E+00	1.06E+05	8.00E+04	8.14E+04	-3.58E+04	-8.36E+00	-2.28E-02	-2.59E-04	-8.00E+04
NO3 -1	9.81E-02	1.83E+00	5.69E-04	1.01E-01	2.94E-01	1.97E-01	2.27E-01	-1.07E-01	-7.97E-02	-1.24E-07	-6.32E-10	-1.97E-01
CRO4 -2	4.76E+04	1.80E+02	1.12E+02	2.36E+00	1.43E+05	9.44E+04	-1.12E+00	-4.84E+04	-1.10E+01	-2.67E-02	-3.03E-04	-9.44E+04
ELECTRNS	1.77E+04	6.71E+01	4.18E+01	8.79E-01	5.32E+04	3.52E+04	4.11E+04	-1.80E+04	-4.11E+00	-9.95E-03	-1.13E-04	-3.52E+04

	NO3 -1	CRO4 -2	ELECTRNS
H +1	9.81E-02	4.76E+04	1.77E+04
CA +2	1.83E+00	1.80E+02	6.71E+01
MG +2	5.69E-04	1.12E+02	4.18E+01
NA +1	1.01E-01	2.36E+00	8.79E-01
FE +3	2.94E-01	1.43E+05	5.32E+04
ZN +2	1.97E-01	9.44E+04	3.52E+04
CR +3	2.27E-01	-1.12E+00	4.11E+04
CO3 -2	-1.07E-01	-4.84E+04	-1.80E+04
SO4 -2	-7.97E-02	-1.10E+01	-4.11E+00
CL -1	-1.24E-07	-2.67E-02	-9.95E-03
I -1	-6.32E-10	-3.03E-04	-1.13E-04
SIO3 -2	-1.97E-01	-9.44E+04	-3.52E+04
NO3 -1	-2.23E+04	-2.63E-01	-9.81E-02
CRO4 -2	-2.63E-01	-1.12E+00	-4.76E+04
ELECTRNS	-9.81E-02	-4.76E+04	-1.77E+04

FIGURE B11E.

INTERACTION INTENSITIES CASE 1

	CA +2	MG +2	NA +1	FE +3	ZN +2	CR +3	CO3 -2	SO4 -2	CL -1	I -1	SIO3 -2	NO3 -1
H +1	4.88E-02	9.63E-03	1.01E-04	6.15E-03	1.28E-02	3.67E-04	-3.22E+01	-2.92E-04	-8.89E-07	-2.01E-12	-3.14E+00	-4.39E-06
CA +2	1.00E+00	9.50E-05	1.27E-06	2.32E-05	4.84E-05	1.39E-06	-1.32E-01	-4.25E-03	-3.55E-09	-7.60E-15	-1.19E-02	-8.18E-05
MG +2	3.00E-04	1.00E+00	9.80E-07	1.45E-05	3.02E-05	8.65E-07	-8.34E-02	-3.55E-03	-3.27E-06	-4.74E-15	-7.41E-03	-2.55E-08
NA +1	8.04E-06	1.95E-06	1.00E+00	3.04E-07	6.34E-07	1.82E-08	-1.64E-03	-1.24E-04	-5.06E-07	-9.96E-17	-1.56E-04	-4.50E-06
FE +3	1.47E-01	2.89E-02	3.04E-04	1.04E-02	3.84E-02	1.10E-03	-9.66E+01	-8.76E-04	-2.67E-06	-6.03E-12	-9.43E+00	-1.32E-05
ZN +2	9.68E-02	1.91E-02	2.01E-04	1.22E-02	2.94E-02	7.28E-04	-6.38E+01	-5.94E-04	-2.03E-06	-4.62E-12	-7.23E+00	-8.84E-06
CR +3	1.13E-01	2.23E-02	2.35E-04	1.42E-02	2.96E-02	1.00E+00	-7.45E+01	-6.76E-04	-2.06E-06	-4.66E-12	-7.28E+00	-1.02E-05
CO3 -2	-5.37E-02	-1.08E-02	-1.06E-04	-6.25E-03	-1.30E-02	-3.74E-04	3.37E+01	3.17E-04	9.07E-07	2.04E-12	3.20E+00	4.80E-06
SO4 -2	-4.36E-02	-1.15E-02	-2.02E-04	-1.42E-06	-3.84E-06	-8.51E-08	7.97E-03	1.00E+00	3.79E-08	4.78E-16	7.48E-04	3.57E-06
CL -1	-2.89E-08	-8.43E-06	-6.53E-07	-3.44E-09	-8.28E-09	-2.06E-10	1.81E-05	3.81E-08	1.00E+00	7.51E-19	2.03E-06	5.57E-12
I -1	-3.10E-10	-6.12E-11	-6.44E-13	-3.90E-11	-9.43E-11	-2.33E-12	2.84E-07	1.90E-12	3.76E-15	1.00E+00	2.32E-08	2.83E-14
SIO3 -2	-9.68E-02	-1.91E-02	-2.01E-04	-1.22E-02	-2.94E-02	-7.28E-04	6.38E+01	5.94E-04	2.03E-06	4.62E-12	7.23E+00	8.84E-06
NO3 -1	-1.33E-03	-1.31E-07	-1.16E-05	-3.40E-08	-7.18E-08	-2.03E-09	1.91E-04	5.66E-06	1.11E-11	1.13E-17	1.76E-05	1.00E+00
CRO4 -2	-1.31E-01	-2.58E-02	-2.72E-04	-1.65E-02	-3.44E-02	9.99E-01	8.64E+01	7.83E-04	2.39E-06	5.40E-12	8.44E+00	1.18E-05
ELECTRNS	-4.88E-02	-9.63E-03	-1.01E-04	-6.15E-03	-1.28E-02	-3.67E-04	3.22E+01	2.92E-04	8.89E-07	2.01E-12	3.14E+00	4.39E-06

	CRO4 -2
H +1	0
CA +2	0
MG +2	0
NA +1	0
FE +3	0
ZN +2	0
CR +3	0
CO3 -2	0
SO4 -2	0
CL -1	0
I -1	0
SIO3 -2	0
NO3 -1	0
CRO4 -2	0
ELECTRNS	0

FIGURE B12. UNDEQ--NO SOLIDS ALLOWED

FIGURE B12A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH NO SOLIDS ALLOWED
1   7  8  1  0  0  0  0  0  0 -1
2      1.2E-03
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
```

FIGURE B12B.

CASE 8

USER INPUT DATA

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 45 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-03

THE CONDITIONS FOR THE 1 CASES ARE

	NUMBER	TOTAL CONCENTRATIONS CASE 1
-LOG(MOLES/L)		
METALS		
CA +2	1	3.500
MG +2	2	4.000
NA +1	5	4.300
FE +3	6	7.300
ZN +2	12	6.000
CR +3	19	8.400
LIGANDS		
CO3 -2	1	3.100
SO4 -2	2	4.500
CL -1	3	4.400
I -1	6	8.100
SIO3 -2	12	4.400
NO3 -1	57	4.700
CRO4 -2	59	12.000
FIXED PH		7.950

NO SOLIDS MAY PRECIPITATE.

FIGURE B12C.

CASE NUMBER 1 CASE 1

CASE PROGRESS
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT 17 ITERATIONS.

CHARGE ON SOLUTION (MOLES/LITER) = -2.229E-05

THE SOLUTION CHARGE IMBALANCE EXCEEDS 0.1 PERCENT OF THE IONIC STRENGTH.
DO NOT USE THESE RESULTS FOR INPUT TO OTHER COMPUTER RUNS.

FIGURE B12D.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.859E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.859E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.816E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	8.900E-12
2	MG +2	9.882E-05	4.005	8.475E-05	4.072	1.000E-04	4.000	2.200E-11
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	3.739E-20
6	FE +3	2.077E-18	17.683	1.469E-18	17.833	5.012E-08	7.300	-1.655E-20
12	ZN +2	1.209E-07	6.917	1.037E-07	6.984	1.585E-07	6.800	1.454E-22
19	CR +3	2.354E-15	14.628	1.665E-15	14.779	3.981E-09	8.400	9.264E-23
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	-1.808E-16
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	-9.523E-16
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	1.588E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	-1.519E-24
12	SIO3 -2	3.646E-12	11.438	3.127E-12	11.505	3.981E-05	4.400	2.883E-10
57	NO3 -1	1.993E-05	4.701	1.910E-05	4.717	1.995E-05	4.700	-6.023E-20
59	CRO4 -2	9.687E-13	12.014	8.307E-13	12.081	1.000E-12	12.000	-3.672E-27

FIGURE B12E.

SATURATION OF SOLIDS

CASE 1

SR = IONIZATION PRODUCT X FORMATION CONSTANT. ***** INDICATES PRECIPITATION.

SOLIDS METAL	LIGAND	LOG 1/SR	H	L	H	LOG 1/SR	H	L	H	LOG 1/SR	H	L	H	LOG 1/SR	H	L	H	LOG 1/SR	H	L	H	LOG 1/SR	H	L	H
1 CA +2																									
	1 CO3 -2	.71	1	1	0	.77	1	1	0																
	2 SO4 -2	3.52	1	1	0	3.31	1	1	0																
	12 SIO3 -2	7.88	1	1	0																				
	99 OH -1	10.48	1	0	-2																				
2 MG +2																									
	1 CO3 -2	2.12	1	1	0	4.91	1	1	0	5.84	1	1	0	7.76	2	1	-2	17.73	5	4	-2				
	12 SIO3 -2	5.29	1	1	0	10.43	2	1	-2	8.27	3	2	-2	10.71	3	4	2	9.61	2	3	2	12.48	2	3	2
	99 OH -1	5.81	1	0	-2																				
5 NA +1																									
	1 CO3 -2	12.83	2	1	0	14.27	2	1	0	6.90	1	1	1	20.80	3	2	1								
	2 SO4 -2	13.85	2	1	0	12.12	2	1	0																
	3 CL -1	10.31	1	1	0																				
	12 SIO3 -2	22.56	1	7	13																				
6 FE +3																									
	99 OH -1	-2.82	1	0	-3	-5.22	1	0	-3	-16.84	2	0	-6	-5.64	2	0	-6								
12 ZN +2																									
	1 CO3 -2	2.50	1	1	0																				
	3 CL -1	9.74	2	1	-3																				
	12 SIO3 -2	-.81	1	1	0																				
	99 OH -1	3.58	1	0	-2	2.41	1	0	-2	2.83	1	0	-2	2.87	1	0	-2	2.81	1	0	-2	2.92	1	0	-2
		2.61	1	0	-2																				
19 CR +3																									
	99 OH -1	1.93	1	0	-3																				
50 H +1																									
	12 SIO3 -2	1.66	0	1	2	.92	0	1	2	.85	0	1	2	.43	0	1	2								

FIGURE B13. UNDEQ--SOLIDS ASSUMED PRESENT

FIGURE B13A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH SOLIDS ASSUMED PRESENT
1   7  8  1  0  0  0  0  0  0  3
2      1.2E-03
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
91212-1 699 1 1 2 1
```

FIGURE B138.

```
U   U  M   M  DDDD   EEEEE   QQQ
U   U  MM MM  D   D  E      Q   Q
U   U  M M M  D   D  E      Q   Q
U   U  M   M  D   D  EEE    Q   Q
U   U  M   M  D   D  E      Q   Q
U   U  M   M  D   D  E      Q  QQ
 UUU   M   M  DDDD   EEEEE   QQQQ
```

UMDEQ VERSION 4.01.00

DATE 81/07/12. TIME 14.54.21.

USING THERMODYNAMIC DATA BASE OF 00/00/01
WHICH CONTAINS THERMODYNAMIC DATA FOR 25.00 DEGREES (C)

SHORT LAKE SUPERIOR DATA WITH SOLIDS ASSUMED PRESENT 2/1/80

THE FOLLOWING SOLIDS ARE DISALLOWED FOR ALL CASES

ZN +2 SIO3 -2 1 1 0

FIGURE B13C.

USER INPUT DATA CASE 0

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 45 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-03

THE CONDITIONS FOR THE 1 CASES ARE

	NUMBER	TOTAL CONCENTRATIONS CASE 1
-LOG(MOLES/L)		
METALS		
CA +2	1	3.500
MG +2	2	4.000
NA +1	5	4.300
FE +3	6	7.300
ZN +2	12	6.000
CR +3	19	8.400
LIGANDS		
CO3 -2	1	3.100
SO4 -2	2	4.500
CL -1	3	4.400
I -1	6	8.100
SIO3 -2	12	4.400
NO3 -1	57	4.700
CRO4 -2	59	12.000
FIXED PH		7.950

THE FOLLOWING 2 SOLIDS ARE ASSUMED *PRESENT INITIALLY:

CA +2	SO4 -2	1	1	0
FE +3	OH -1	1	0	-3

FIGURE B13D.

CASE NUMBER 1


```
CASE PROGRESS
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  17 ITERATIONS.
SOLID  CA +2    SO4 -2    1 1 0  DISSOLVES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  19 ITERATIONS.
SOLID  FE +3    OH -1     1 0-3  DISSOLVES.
SOLID  FE +3    OH -1     2 0-6  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  20 ITERATIONS.

  CHARGE ON SOLUTION (MOLES/LITER) = -2.229E-05

    THE SOLUTION CHARGE IMBALANCE EXCEEDS 0.1 PERCENT OF THE IONIC STRENGTH.
DO NOT USE THESE RESULTS FOR INPUT TO OTHER COMPUTER RUNS.
```

FIGURE 813E.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.280E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.859E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.816E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	4.713E-10
2	MG +2	9.882E-05	4.005	8.475E-05	4.072	1.000E-04	4.000	-4.759E-12
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-2.901E-15
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.209E-07	6.917	1.037E-07	6.984	1.585E-07	6.800	-8.386E-15
19	CR +3	2.354E-15	14.628	1.665E-15	14.779	3.981E-09	8.400	-2.978E-22
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	-4.140E-13
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	4.669E-10
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-1.011E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	7.096E-24
12	SIO3 -2	3.646E-12	11.438	3.127E-12	11.505	3.981E-05	4.400	8.972E-10
57	NO3 -1	1.993E-05	4.701	1.918E-05	4.717	1.995E-05	4.700	-1.157E-15
59	CRO4 -2	9.687E-13	12.014	8.307E-13	12.081	1.000E-12	12.000	-1.216E-25

SOLID					HOLES PER LITER OF SOLUTION
FE +3	OH -1	2	8	-6	2.586E-08

FIGURE B13F.

SATURATION OF SOLIDS

CASE 1

SR = IONIZATION PRODUCT X FORMATION CONSTANT. ***** INDICATES PRECIPITATION.

SOLIDS METAL	LIGAND	LOG 1/SR	H	L	H	LOG 1/SR	H	L	H	LOG 1/SR	H	L	H	LOG 1/SR	H	L	H	LOG 1/SR	H	L	H	LOG 1/SR	H	L	H
1 CA +2																									
	1 CO3 -2	.71	1	1	0	.77	1	1	0																
	2 SO4 -2	3.52	1	1	0	3.31	1	1	0																
	12 SIO3 -2	7.88	1	1	0																				
	99 OH -1	18.48	1	0	-2																				
2 MG +2																									
	1 CO3 -2	2.12	1	1	0	4.91	1	1	0	5.84	1	1	0	7.76	2	1	-2	17.73	5	4	-2				
	12 SIO3 -2	5.29	1	1	0	10.43	2	1	-2	8.27	3	2	-2	18.71	3	4	2	9.61	2	3	2	12.48	2	3	2
	99 OH -1	5.81	1	0	-2																				
5 NA +1																									
	1 CO3 -2	12.83	2	1	0	14.27	2	1	0	6.98	1	1	1	20.88	3	2	1								
	2 SO4 -2	13.05	2	1	0	12.12	2	1	0																
	3 CL -1	18.31	1	1	0																				
	12 SIO3 -2	22.56	1	7	13																				
6 FE +3																									
	99 OH -1	5.20	1	0	-3	2.88	1	0	-3	*******	2	0	-6	10.40	2	0	-6								
12 ZN +2																									
	1 CO3 -2	2.50	1	1	0																				
	3 CL -1	9.74	2	1	-3																				
	12 SIO3 -2	-.01	1	1	0																				
	99 OH -1	3.58	1	0	-2	2.41	1	0	-2	2.83	1	0	-2	2.87	1	0	-2	2.81	1	0	-2	2.92	1	0	-2
19 CR +3		2.61	1	0	-2																				
	99 OH -1	1.93	1	0	-3																				
50 H +1																									
	12 SIO3 -2	1.66	0	1	2	.92	0	1	2	.85	0	1	2	.43	0	1	2								

FIGURE B14. UMDEQ--MIXED SOLIDS

FIGURE B14A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH MIXED SOLIDS
1   7  8  1  0  0  0  0  0  0  0  1
2      1.2E-03
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
```

FIGURE B14B.

UNCORRECTED THERMODYNAMIC DATA FOR VERIFICATION

CASE 0

SOLIDS

METAL	LIGAND	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
1 CA +2																									
	1 CO3 -2	8.37	1	1	0	8.31	1	1	0																
	2 SO4 -2	4.64	1	1	0	4.85	1	1	0																
	12 SIO3 -2	7.20	1	1	0																				
	99 OH -1	-22.81	1	0	-2																				
2 MG +2																									
	1 CO3 -2	7.46	1	1	0	4.67	1	1	0	4.54	1	1	0	-18.01	2	1	-2	8.77	5	4	-2				
	12 SIO3 -2	18.29	1	1	0	-6.68	2	1	-2	11.86	3	2	-2	63.43	3	4	2	48.95	2	3	2	46.88	2	3	2
	99 OH -1	-16.84	1	0	-2																				
5 NA +1																									
	1 CO3 -2	1.31	2	1	0	-.13	2	1	0	10.88	1	1	1	11.12	3	2	1								
	2 SO4 -2	.18	2	1	0	1.11	2	1	0																
	3 CL -1	-1.58	1	1	0																				
	12 SIO3 -2	165.64	1	7	13																				
6 FE +3																									
	99 OH -1	-3.20	1	0	-3	-.88	1	0	-3	4.01	2	0	-6	-6.39	2	0	-6								
12 ZN +2																									
	1 CO3 -2	10.00	1	1	0																				
	3 CL -1	-15.20	2	1	-3																				
	12 SIO3 -2	18.50	1	1	0																				
	99 OH -1	-12.50	1	0	-2	-11.33	1	0	-2	-11.75	1	0	-2	-11.79	1	0	-2	-11.73	1	0	-2	-11.84	1	0	-2
		-11.53	1	0	-2																				
19 CR +3																									
	99 OH -1	-11.00	1	0	-3																				
50 H +1																									
	12 SIO3 -2	25.74	0	1	2	26.48	0	1	2	26.55	0	1	2	26.97	0	1	2								

MIXED SOLIDS

NAME	LOG K	H+/OH-			
DOLOMITE	17.00	0	1*CA +2	1*MG +2	2*CO3 -2
HUNTITE	30.00	0	1*CA +2	3*MG +2	4*CO3 -2

COMPLEXES

METAL	LIGAND	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
1 CA +2																									
	1 CO3 -2	3.15	1	1	0	11.33	1	1	1																
	2 SO4 -2	2.31	1	1	0																				
	12 SIO3 -2	3.09	1	1	0	13.50	1	1	1	29.10	1	2	2												
	57 NO3 -1	.70	1	1	0	.60	1	2	0																
	99 OH -1	-12.65	1	0	-1																				
2 MG +2																									
	1 CO3 -2	2.00	1	1	0	11.20	1	1	1																

CASE 0

	2 SO4 -2	2.23	1	1	0																								
	3 CL -1	-1.00	1	1	0																								
	12 SIO3 -2	4.17	1	1	0	13.70	1	1	1	30.00	1	2	2																
5 NA +1	99 OH -1	-11.44	1	0	-1	-39.71	4	0	-4																				
	1 CO3 -2	1.20	1	1	0																								
	2 SO4 -2	.70	1	1	0																								
	3 CL -1	-1.85	1	1	0																								
	57 NO3 -1	-.60	1	1	0																								
	99 OH -1	-14.18	1	0	-1																								
6 FE +3																													
	2 SO4 -2	4.04	1	1	0	5.38	1	2	0																				
	3 CL -1	1.48	1	1	0	2.13	1	2	0	1.30	1	3	0																
	6 I -1	3.50	1	1	0	2.40	1	2	0																				
	12 SIO3 -2	22.60	1	1	1																								
	57 NO3 -1	1.00	1	1	0																								
	59 CRO4 -2	7.01	1	1	0																								
	99 OH -1	-2.19	1	0	-1	-5.67	1	0	-2	-21.60	1	0	-4	-2.95	2	0	-2	-6.30	3	0	-4								
12 ZN +2																													
	1 CO3 -2	4.70	1	1	0																								
	2 SO4 -2	2.30	1	1	0	3.20	1	2	0	1.70	1	3	0	1.70	1	4	0												
	3 CL -1	.43	1	1	0	.61	1	2	0	.50	1	3	0	.20	1	4	0												
	6 I -1	-1.50	1	1	0	-1.76	1	2	0	-1.03	1	3	0	-2.42	1	4	0												
	57 NO3 -1	.40	1	1	0	-.30	1	2	0																				
	99 OH -1	-8.96	1	0	-1	-28.40	1	0	-3	-41.20	1	0	-4	-16.90	1	0	-2	-9.00	2	0	-1								
19 CR +3																													
	2 SO4 -2	2.70	1	1	0																								
	3 CL -1	.00	1	1	0	.01	1	2	0																				
	99 OH -1	-4.00	1	0	-1	-9.70	1	0	-2	-27.40	1	0	-4	-5.06	2	0	-2	-8.15	3	0	-4	-18.00	1	0	-3				
50 H +1																													
	1 CO3 -2	18.33	0	1	1	16.60	0	1	2																				
	2 SO4 -2	1.99	0	1	1																								
	12 SIO3 -2	13.10	0	1	1	23.00	0	1	2	55.90	0	4	4	74.20	0	4	6												
	59 CRO4 -2	6.51	0	1	1	14.55	0	2	2	6.31	0	1	2																

MIXED COMPLEXES

MET	LIG	IONS	LOG K M L I3 H	LOG K M L I3 H	LOG K M L I3 H	LOG K M L I3 H	LOG K M L I3 H
ZN +2	CL -1	I -1	.99 1 2 1 0	.69 1 1 2 0	1.51 1 3 1 0	1.11 1 2 2 0	

FIGURE B14C.

CASE NUMBER 1


```
CASE PROGRESS
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  17 ITERATIONS.
SOLID  FE +3    OH -1      2 0-6  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  18 ITERATIONS.
SOLID  ZN +2    SIO3 -2   1 1 0  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  21 ITERATIONS.

  CHARGE ON SOLUTION (MOLES/LITER) = -2.230E-05

    THE SOLUTION CHARGE IMBALANCE EXCEEDS 0.1 PERCENT OF THE IONIC STRENGTH.
DO NOT USE THESE RESULTS FOR INPUT TO OTHER COMPUTER RUNS.
```

FIGURE B14D.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.208E-03

FIXED PH = 7.950
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.859E-04 POH = 6.050
-LOG KH = 13.967
H+ ION CONCENTRATION = 7.933 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
CARBONATE ALKALINITY = 7.816E-04 OH- ION CONCENTRATION = 6.033

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	1.232E-16
2	MG +2	9.882E-05	4.005	8.475E-05	4.072	1.060E-04	4.000	6.330E-17
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-3.389E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.180E-07	6.928	1.012E-07	6.995	1.585E-07	6.800	-1.582E-11
19	CR +3	2.354E-15	14.628	1.665E-15	14.779	3.981E-09	8.400	1.191E-22
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	4.337E-17
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	-2.050E-19
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-6.422E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	-8.936E-24
12	SIO3 -2	3.646E-12	11.438	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.993E-05	4.701	1.918E-05	4.717	1.995E-05	4.700	5.075E-20
59	CRO4 -2	9.687E-13	12.014	8.307E-13	12.081	1.000E-12	12.000	-1.249E-27

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	3.074E-09

FIGURE B15. UMDEQ--MIXED SOLID, DOLOMITE, DISALLOWED

FIGURE B15A. INPUT CARDS.

```
0  SHORT LAKE SUPERIOR DATA WITH MIXED SOLIDS BUT DOLOMITE DISALLOWED
1   7  8  1  0  0  0  0  0  0  0  2
2      1.2E-03
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
```

FIGURE B15B.

```
U   U  M   M  DDDD   EEEEE   QQQ        UMDEQ VERSION  4.01.80
U   U  MM MM  D   D  E      Q   Q
U   U  M M M  D   D  E      Q   Q        DATE  81/07/12.    TIME  15.05.57.
U   U  M   M  D   D  EEE    Q   Q
U   U  M   M  D   D  E      Q   Q        USING THERMODYNAMIC DATA BASE OF 80/08/01
U   U  M   M  D   D  E      Q  QQ        WHICH CONTAINS THERMODYNAMIC DATA FOR 25.00 DEGREES (C)
 UUU   M   M  DDDD   EEEEE   QQQQ
```

SHORT LAKE SUPERIOR DATA WITH MIXED SOLIDS BUT DOLOMITE DISALLOWED 2/1/80

THE FOLLOWING MIXED SOLIDS ARE DISALLOWED:

DOLOMITE

FIGURE B15C.

USER INPUT DATA

CASE 0

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 45 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-03

THE CONDITIONS FOR THE 1 CASES ARE

	NUMBER	TOTAL CONCENTRATIONS CASE 1
-LOG(MOLES/L)		
METALS		
CA +2	1	3.500
MG +2	2	4.000
NA +1	5	4.300
FE +3	6	7.300
ZN +2	12	6.800
CR +3	19	8.400
LIGANDS		
CO3 -2	1	3.100
SO4 -2	2	4.500
CL -1	3	4.400
I -1	6	8.100
SIO3 -2	12	4.400
NO3 -1	57	4.700
CRO4 -2	59	12.000
FIXED PH		7.950

FIGURE B15D.

CASE 0

THERMODYNAMIC DATA AFTER IONIC STRENGTH CORRECTIONS WITH MAGNUSON EQUATION.

SOLIDS

METAL	LIGAND	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
1 CA +2																									
	1 CO3 -2	8.24	1	1	0	8.18	1	1	0																
	2 SO4 -2	4.51	1	1	0	4.72	1	1	0																
	12 SIO3 -2	7.07	1	1	0																				
	99 OH -1	-22.84	1	0	-2																				
2 MG +2																									
	1 CO3 -2	7.33	1	1	0	4.54	1	1	0	4.41	1	1	0	-10.18	2	1	-2	8.20	5	4	-2				
	12 SIO3 -2	10.16	1	1	0	-6.85	2	1	-2	10.76	3	2	-2	62.93	3	4	2	48.58	2	3	2	45.71	2	3	2
	99 OH -1	-16.87	1	0	-2																				
5 NA +1																									
	1 CO3 -2	1.21	2	1	0	-.23	2	1	0	10.78	1	1	1	10.92	3	2	1								
	2 SO4 -2	.88	2	1	0	1.81	2	1	0																
	3 CL -1	-1.61	1	1	0																				
	12 SIO3 -2	164.94	1	7	13																				
6 FE +3																									
	99 OH -1	-3.38	1	0	-3	-.98	1	0	-3	3.81	2	0	-6	-6.59	2	0	-6								
12 ZN +2																									
	1 CO3 -2	9.87	1	1	0																				
	3 CL -1	-15.38	2	1	-3																				
	12 SIO3 -2	18.37	1	1	0																				
	99 OH -1	-12.53	1	0	-2	-11.36	1	0	-2	-11.78	1	0	-2	-11.82	1	0	-2	-11.76	1	0	-2	-11.87	1	0	-2
		-11.56	1	0	-2																				
19 CR +3																									
	99 OH -1	-11.18	1	0	-3																				
50 H +1																									
	12 SIO3 -2	25.64	0	1	2	26.38	0	1	2	26.45	0	1	2	26.87	0	1	2								

MIXED SOLIDS

NAME	LOG K	H+/OH-			
DOLOMITE	16.73	0	1*CA +2	1*MG +2	2*CO3 -2
HUNTITE	29.47	0	1*CA +2	3*MG +2	4*CO3 -2

COMPLEXES

METAL	LIGAND	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H	LOG K	M	L	H
1 CA +2																									
	1 CO3 -2	3.02	1	1	0	11.28	1	1	1																
	2 SO4 -2	2.18	1	1	0																				
	12 SIO3 -2	2.96	1	1	0	13.37	1	1	1	28.87	1	2	2												
	57 NO3 -1	.63	1	1	0	.58	1	2	0																
	99 OH -1	-12.88	1	0	-1																				
2 MG +2																									
	1 CO3 -2	2.75	1	1	0	11.15	1	1	1																

CASE 0

	2	SO4 -2	2.18	1	1	0																													
	3	CL -1	-1.87	1	1	0																													
	12	SIO3 -2	4.84	1	1	0	13.57	1	1	1	29.77	1	2	2																					
	99	OH -1	-11.47	1	0	-1	-39.64	4	0	-4																									
5 NA +1																																			
	1	CO3 -2	1.13	1	1	0																													
	2	SO4 -2	.63	1	1	0																													
	3	CL -1	-1.88	1	1	0																													
	57	NO3 -1	-.63	1	1	0																													
	99	OH -1	-14.18	1	0	-1																													
6 FE +3																																			
	2	SO4 -2	3.84	1	1	0	5.11	1	2	0																									
	3	CL -1	1.38	1	1	0	1.96	1	2	0	1.18	1	3	0																					
	6	I -1	3.40	1	1	0	2.23	1	2	0																									
	12	SIO3 -2	22.43	1	1	1																													
	57	NO3 -1	.98	1	1	0																													
	59	CRO4 -2	7.61	1	1	0																													
	99	OH -1	-2.26	1	0	-1	-5.77	1	0	-2	-21.67	1	0	-4	-2.95	2	0	-2	-6.27	3	0	-4													
12 ZN +2																																			
	1	CO3 -2	4.57	1	1	0																													
	2	SO4 -2	2.25	1	1	0	3.87	1	2	0	1.78	1	3	0	1.97	1	4	0																	
	3	CL -1	.36	1	1	0	.51	1	2	0	.48	1	3	0	.13	1	4	0																	
	6	I -1	-1.57	1	1	0	-1.86	1	2	0	-1.93	1	3	0	-2.49	1	4	0																	
	57	NO3 -1	.33	1	1	0	-.40	1	2	0																									
	99	OH -1	-8.99	1	0	-1	-20.40	1	0	-3	-41.13	1	0	-4	-16.93	1	0	-2	-8.97	2	0	-1													
19 CR +3																																			
	2	SO4 -2	2.50	1	1	0																													
	3	CL -1	.70	1	1	0	-.16	1	2	0																									
	99	OH -1	-4.07	1	0	-1	-9.80	1	0	-2	-27.47	1	0	-4	-5.86	2	0	-2	-8.12	3	0	-4	-18.10	1	0	-3									
53 H +1																																			
	1	CO3 -2	18.26	0	1	1	16.58	0	1	2																									
	2	SO4 -2	1.92	0	1	1																													
	12	SIO3 -2	13.03	0	1	1	22.90	0	1	2	55.83	0	4	4	77.98	0	4	6																	
	59	CRO4 -2	6.44	0	1	1	14.45	0	2	2	6.21	0	1	2																					

MIXED COMPLEXES

MET	LIG	IONS	LOG K M L I3 H	LOG K M L I3 H	LOG K M L I3 H	LOG K M L I3 H	LOG K M L I3 H
ZN +2	CL -1	I -1	.89 1 2 1 0	.59 1 1 2 0	1.44 1 3 1 0	1.84 1 2 2 0	

FIGURE B15E.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.208E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.859E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.816E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	1.232E-16
2	MG +2	9.802E-05	4.005	8.475E-05	4.072	1.000E-04	4.000	6.330E-17
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-3.389E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.100E-07	6.928	1.012E-07	6.995	1.585E-07	6.800	-1.582E-11
19	CR +3	2.354E-15	14.628	1.665E-15	14.779	3.981E-09	8.400	1.191E-22
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	4.337E-17
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	-2.050E-19
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-6.422E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	-8.936E-24
12	SIO3 -2	3.646E-12	11.438	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.993E-05	4.701	1.918E-05	4.717	1.995E-05	4.700	5.075E-20
59	CRO4 -2	9.607E-13	12.014	8.307E-13	12.081	1.000E-12	12.000	-1.249E-27

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	3.874E-09

FIGURE B16. UNDEQ--MG/L INPUT

FIGURE B16A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH MG/L INPUT
1   7  8  1  0  0  0  0  0  0  0  0  1
2      1.2E-03
3  1  55   126+01
3  2  60   2.432
3  5  63   115+00
3  6  93    .0028
3 12  88    .0104
3 19 104   207-04
4  1  51    47.7
4  2  65    3.04
4  3  64    1.41
4  6 101   .00101
4 12  64   1.118
4 57  67   .2794
4 59 140   5.19-8
5     795
```

FIGURE 0160.

USER INPUT DATA

CASE 0

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 45 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-03

THE CONDITIONS FOR THE 1 CASES ARE

	NUMBER	TOTAL CONCENTRATIONS CASE 1
MG/L		
METALS		
CA +2	1	1.260E+01
MG +2	2	2.432E+00
NA +1	5	1.150E+00
FE +3	6	2.800E-03
ZN +2	12	1.040E-02
CR +3	19	2.070E-04
LIGANDS		
CO3 -2	1	4.770E+01
SO4 -2	2	3.040E+00
CL -1	3	1.410E+00
I -1	6	1.010E-03
SIO3 -2	12	1.110E+00
NO3 -1	57	2.794E-01
CRO4 -2	59	5.190E-00

-LOG(MOLES/L)		
METALS		
CA +2	1	3.503
MG +2	2	4.000
NA +1	5	4.301
FE +3	6	7.300
ZN +2	12	6.790
CR +3	19	8.400
LIGANDS		
CO3 -2	1	3.106
SO4 -2	2	4.500
CL -1	3	4.400
I -1	6	8.099
SIO3 -2	12	4.400
NO3 -1	57	4.700
CRO4 -2	59	12.041
FIXED PH		7.950

FIGURE B16C.

CASE NUMBER 1


```
CASE PROGRESS
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  58 ITERATIONS.
SOLID  FE +3    OH -1      2 8-6  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  59 ITERATIONS.
SOLID  ZN +2    SIO3 -2    1 1 0  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  62 ITERATIONS.

  CHARGE ON SOLUTION (MOLES/LITER) = -2.662E-05

    THE SOLUTION CHARGE IMBALANCE EXCEEDS 0.1 PERCENT OF THE IONIC STRENGTH.
DO NOT USE THESE RESULTS FOR INPUT TO OTHER COMPUTER RUNS.
```

FIGURE B16D.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.865E-04 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.867E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.822E-04

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.098E-04	3.509	2.656E-04	3.576	3.144E-04	3.503	2.359E-16
2	MG +2	9.882E-05	4.005	8.475E-05	4.072	1.000E-04	4.000	1.222E-16
5	NA +1	5.001E-05	4.301	4.813E-05	4.318	5.002E-05	4.301	6.200E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.013E-08	7.300	0
12	ZN +2	1.179E-07	6.929	1.011E-07	6.995	1.590E-07	6.798	-3.058E-11
19	CR +3	2.353E-15	14.628	1.665E-15	14.779	3.980E-09	8.400	3.838E-22
1	CO3 -2	3.597E-06	5.444	3.084E-06	5.511	7.949E-04	3.100	3.578E-17
2	SO4 -2	2.988E-05	4.525	2.562E-05	4.591	3.164E-05	4.500	-2.451E-19
3	CL -1	3.977E-05	4.400	3.827E-05	4.417	3.977E-05	4.400	1.069E-19
6	I -1	7.958E-09	8.099	7.660E-09	8.116	7.958E-09	8.099	9.390E-24
12	SIO3 -2	3.649E-12	11.438	3.129E-12	11.505	3.984E-05	4.400	0
57	NO3 -1	1.992E-05	4.701	1.917E-05	4.717	1.995E-05	4.700	-2.077E-20
59	CRO4 -2	8.818E-13	12.055	7.562E-13	12.121	9.104E-13	12.041	9.048E-28

SOLID						MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6		2.507E-08
ZN +2	SIO3 -2	1	1	4		4.552E-09

FIGURE B17. UMDEQ--N2 REDOX

FIGURE B17A. INPUT CARDS

```
0  SHORT LAKE SUPERIOR DATA WITH N2 PRESENT  2
1   7  8  5  0  0  0  0  0  1
2      1.2E-03
3  1  55    35
3  2  60    40
3  5  63    43
3  6  93    73
3 12  88    68
3 19 104    84
4  1  51    31
4  2  65    45
4  3  64    44
4  6 101    81
4 12  64    44
4 57  67    47
4 59 140   120
5     795
7    120    80    40    00   -40
```

FIGURE B17B.

USER INPUT DATA

CASE 8

THESE COMPUTATIONS INVOLVE 7 METALS AND 8 LIGANDS
FORMING 81 COMPLEXES AND 47 POSSIBLE SOLIDS.

IONIC STRENGTH WILL NOT CHANGE.
IONIC STRENGTH = 1.200E-03

THE CONDITIONS FOR THE 5 CASES ARE

	NUMBER	TOTAL CONCENTRATIONS CASE 1	CASE 2	CASE 3	CASE 4	CASE 5
-LOG(MOLES/L)						
METALS						
CA +2	1	3.500	3.500	3.500	3.500	3.500
MG +2	2	4.000	4.000	4.000	4.000	4.000
NA +1	5	4.300	4.300	4.300	4.300	4.300
FE +3	6	7.300	7.300	7.300	7.300	7.300
ZN +2	12	6.800	6.800	6.800	6.800	6.800
CR +3	19	8.400	8.400	8.400	8.400	8.400
LIGANDS						
CO3 -2	1	3.100	3.100	3.100	3.100	3.100
SO4 -2	2	4.500	4.500	4.500	4.500	4.500
CL -1	3	4.400	4.400	4.400	4.400	4.400
I -1	6	8.100	8.100	8.100	8.100	8.100
SIO3 -2	12	4.400	4.400	4.400	4.400	4.400
NO3 -1	57	4.700	4.700	4.700	4.700	4.700
CRO4 -2	59	12.000	12.000	12.000	12.000	12.000
FIXED PH		7.950	7.950	7.950	7.950	7.950
REDOX POTENTIAL		12.000	8.000	4.000	0	-4.000
N2 PRESSURE		.100	.100	.100	.100	.100

THE FOLLOWING REDOX REACTIONS ARE CONSIDERED

N2(G) FE3O4 CR3/CRO4

FIGURE B17C.

CASE NUMBER 1

```
CASE PROGRESS                                                                    CASE  1
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  17 ITERATIONS.
SOLID  H  +1    NO3 -1    0 212  DISSOLVES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  19 ITERATIONS.
SOLID  FE +3    OH -1     2 0-6  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  20 ITERATIONS.
SOLID  ZN +2    SIO3 -2   1 1 0  PRECIPITATES.
SOLUTIONS FOR CONSERVATION OF MASS CONVERGE AT  23 ITERATIONS.

  CHARGE ON SOLUTION (MOLES/LITER) = -2.232E-05

   THE SOLUTION CHARGE IMBALANCE EXCEEDS 0.1 PERCENT* OF THE IONIC STRENGTH.
DO NOT USE THESE RESULTS FOR INPUT TO OTHER COMPUTER RUNS.
 *
```

FIGURE B17D.

FINAL ION AND SOLID CONCENTRATIONS

CASE 1

FINAL IONIC STRENGTH = 1.208E-03

FIXED PH = 7.950
POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 8.859E-04
SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933
OH- ION CONCENTRATION = 6.833
CARBONATE ALKALINITY = 7.816E-04

FIXED PE = 12.00

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	1.223E-16
2	MG +2	9.802E-05	4.005	8.475E-05	4.072	1.000E-04	4.000	6.309E-17
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-2.968E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.180E-07	6.928	1.012E-07	6.995	1.585E-07	6.800	-1.582E-11
19	CR +3	9.329E-34	33.030	6.600E-34	33.180	0	******	0
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	-5.378E-17
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	-8.451E-20
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-9.997E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	-8.936E-24
12	SIO3 -2	3.646E-12	11.438	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	1.993E-05	4.701	1.918E-05	4.717	1.995E-05	4.700	5.075E-20
59	CRO4 -2	3.857E-09	8.414	3.308E-09	8.480	3.982E-09	8.400	0

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	3.874E-09

FIGURE B17E.

FINAL ION AND SOLID CONCENTRATIONS

CASE 2

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 1.006E-03 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.816E-04

FIXED PE = 8.00
LOG FORMATION CONSTANT FOR N2 = 218.05

-LOG PARTIAL PRESSURE OF PN2 = .10

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	-2.668E-08
2	MG +2	9.082E-05	4.085	8.475E-05	4.072	1.060E-04	4.000	6.309E-17
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-2.323E-10
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.180E-07	6.928	1.012E-07	6.995	1.585E-07	6.800	-2.088E-11
19	CR +3	9.329E-22	21.030	6.600E-22	21.180	1.570E-15	14.802	1.570E-15
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	-5.370E-17
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	-8.451E-20
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	-9.997E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	-8.936E-24
12	SIO3 -2	3.646E-12	11.430	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	3.362E-18	17.473	3.236E-18	17.490	1.995E-05	4.700	0
59	CRO4 -2	3.857E-09	8.414	3.308E-09	8.480	3.982E-09	8.400	1.570E-15

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	3.874E-09
H +1	NO3 -1	0	2	12	9.976E-06

FIGURE B17F.

FINAL ION AND SOLID CONCENTRATIONS

CASE 3

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 1.006E-03 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.816E-04

FIXED PE = 4.00
LOG FORMATION CONSTANT FOR N2 = 210.05

-LOG PARTIAL PRESSURE OF PN2 = .10

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	6.085E-19
2	MG +2	9.882E-05	4.005	8.475E-05	4.072	1.000E-04	4.000	-1.532E-19
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-8.065E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.180E-07	6.928	1.012E-07	6.995	1.585E-07	6.800	5.687E-18
19	CR +3	2.354E-15	14.628	1.665E-15	14.778	3.982E-09	8.400	7.843E-22
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	6.408E-17
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	-1.450E-19
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	4.630E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	4.360E-24
12	SIO3 -2	3.646E-12	11.438	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	3.362E-38	37.473	3.236E-38	37.490	1.995E-05	4.700	0
59	CRO4 -2	9.734E-15	14.012	8.347E-15	14.078	1.005E-14	13.998	7.843E-22

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	3.894E-09
H +	NO3 -1	0	2	12	9.976E-06

FIGURE B17G.

FINAL ION AND SOLID CONCENTRATIONS

CASE 4

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 7.950 POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 1.006E-03 SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933 OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.816E-04

FIXED PE = 0
LOG FORMATION CONSTANT FOR H2 = 210.05

-LOG PARTIAL PRESSURE OF PH2 = .10

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	2.020E-19
2	MG +2	9.882E-05	4.005	8.475E-05	4.072	1.000E-04	4.000	-2.548E-19
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-8.097E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.100E-07	6.920	1.012E-07	6.995	1.585E-07	6.800	5.696E-10
19	CR +3	2.354E-15	14.620	1.666E-15	14.770	3.982E-09	8.400	2.392E-13
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	-4.142E-17
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	7.325E-20
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	4.633E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	4.360E-24
12	SIO3 -2	3.646E-12	11.438	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	3.362E-58	57.473	3.236E-58	57.490	1.995E-05	4.700	0
59	CRO4 -2	9.735E-27	26.012	8.348E-27	26.078	1.292E-26	25.889	2.392E-13

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.586E-08
ZN +2	SIO3 -2	1	.	0	3.894E-09
H +1	NO3 -1	0	2	12	9.976E-06

FIGURE B17H.

FINAL ION AND SOLID CONCENTRATIONS

CASE 5

FINAL IONIC STRENGTH = 1.200E-03

FIXED PH = 7.950
POH = 6.050
COMPUTED TOTAL HYDROGEN LESS HYDROXIDE = 1.006E-03
SOLUBLE TOTAL HYDROGEN LESS HYDROXIDE = 8.861E-04
-LOG KW = 13.967
H+ ION CONCENTRATION = 7.933
OH- ION CONCENTRATION = 6.033
CARBONATE ALKALINITY = 7.816E-04

FIXED PE = -4.00
LOG FORMATION CONSTANT FOR N2 = 210.05

-LOG PARTIAL PRESSURE OF PN2 = .10

		FREE CONC MOLES/LITER	-LOG FREE CONC	ACTIVITY MOLES/LITER	-LOG ACTIVITY	TOT CONC MOLES/LITER	-LOG TOT CONC	REMAINDER
1	CA +2	3.116E-04	3.506	2.672E-04	3.573	3.162E-04	3.500	2.020E-19
2	MG +2	9.082E-05	4.085	8.475E-05	4.072	1.000E-04	4.000	-2.548E-19
5	NA +1	5.011E-05	4.300	4.823E-05	4.317	5.012E-05	4.300	-8.097E-20
6	FE +3	1.974E-26	25.705	1.396E-26	25.855	5.012E-08	7.300	0
12	ZN +2	1.180E-07	6.928	1.012E-07	6.995	1.585E-07	6.800	5.696E-18
19	CR +3	2.354E-15	14.628	1.666E-15	14.778	3.982E-09	8.400	2.392E-13
1	CO3 -2	3.594E-06	5.444	3.082E-06	5.511	7.943E-04	3.100	-4.142E-17
2	SO4 -2	2.985E-05	4.525	2.560E-05	4.592	3.162E-05	4.500	7.325E-20
3	CL -1	3.981E-05	4.400	3.832E-05	4.417	3.981E-05	4.400	4.633E-20
6	I -1	7.943E-09	8.100	7.645E-09	8.117	7.943E-09	8.100	4.360E-24
12	SIO3 -2	3.646E-12	11.438	3.126E-12	11.505	3.981E-05	4.400	0
57	NO3 -1	3.362E-78	77.473	3.236E-78	77.490	1.995E-05	4.700	0
59	CRO4 -2	9.735E-39	38.012	8.348E-39	38.078	0	******	2.392E-13

SOLID					MOLES PER LITER OF SOLUTION
FE +3	OH -1	2	0	-6	2.506E-08
ZN +2	SIO3 -2	1	1	0	3.894E-09
H +1	NO3 -1	0	2	12	9.976E-06

APPENDIX C: OXIDATION-REDUCTION REACTIONS

Reference Number	Reaction Type	Log K	Reaction
1	-10	13.0	$Fe^{3+} + e \rightarrow Fe^{2+}$
2	-1	208.9	$2NO_3^- + 12H^+ + 10e \rightarrow N_2(g) + 6H_2O$
3	-2	28.7	$Hg^{2+} + 2e \rightarrow Hg(liq)$
4	-10	30.7	$2Hg^{2+} + 2e \rightarrow Hg_2^{2+}$
5	-2	-49.2	$Pb^{2+} + 2H_2O \rightarrow PbO_2(s) + 4H^+ + 2e$
6	-10	-31.6	$Co^{2+} \rightarrow Co^{3+} + e$
7	3	13.2	$CO_3^{2-} + 6H^+ + 4e \rightarrow CH_2O(aq) + 2H_2O$
8	10	-20.0	$S^{2-} + 4H_2O \rightarrow SO_4^{2-} + 8H^+ + 8e$
9	10	-110.0	$NH_3(aq) + 3H_2O \rightarrow NO_3^- + 9H^+ + 8e$
10	1	-60.1	$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e$
11	-10	-5.1	$Sn^{2+} \rightarrow Sn^{4+} + 2e$
12	-2	45.3	$Fe^{2+} + 2S^{2-} \rightarrow FeS_2(s) + 2e$
13	-2	6.4	$3Fe^{3+} + 4H_2O + e \rightarrow Fe_3O_4(s) + 8H^+$
14	-3	-61.7	$3Mn^{2+} + 4H_2O \rightarrow Mn_3O_4(s) + 8H^+ + 2e$
15	-1	-25.7	$Mn^{2+} + 2H_2O \rightarrow MnO(OH)(s) + 3H^+ + e$
16	-11	-74.9	$Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e$
17	-1	16.2	$S^{2-} \rightarrow S(s) + 2e$
18	10	71.6	$4S^{2-} \rightarrow S_4^{2-} + 6e$
19	10	87.1	$5S^{2-} \rightarrow S_5^{2-} + 8e$
20	-10	-2.6	$Cu^+ \rightarrow Cu^{2+} + e$
21	-1	8.8	$Cu^+ + e \rightarrow Cu(s)$

22	-2	-42.0	$Mn^{2+} + 2H_2O \rightarrow MnO_2(s) + 4H^+ + 2e$

APPENDIX D

pE-pH Plots for Oxidation Reduction

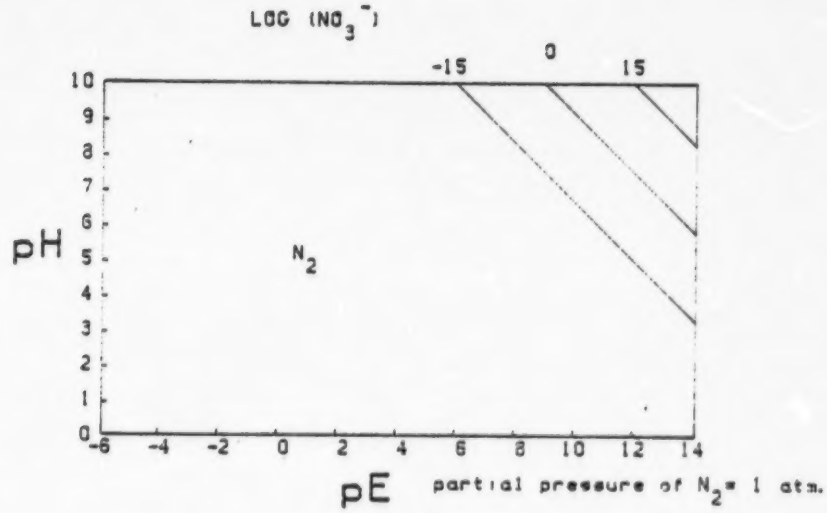


Figure D2. pH-pE. Reaction 2 $2NO_3^- + 12H^+ + 10e^- \longrightarrow N_{2(g)} + 6H_2O$

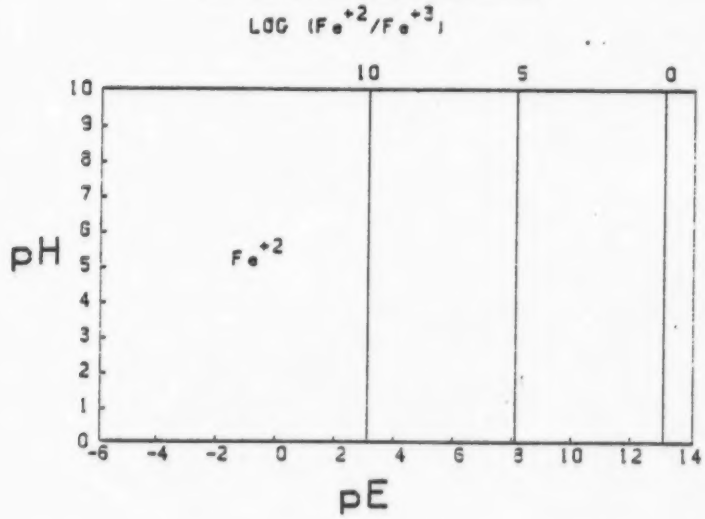


Figure D1. pH-pE. Reaction 1 $Fe^{+3} + e^- \longrightarrow Fe^{+2}$

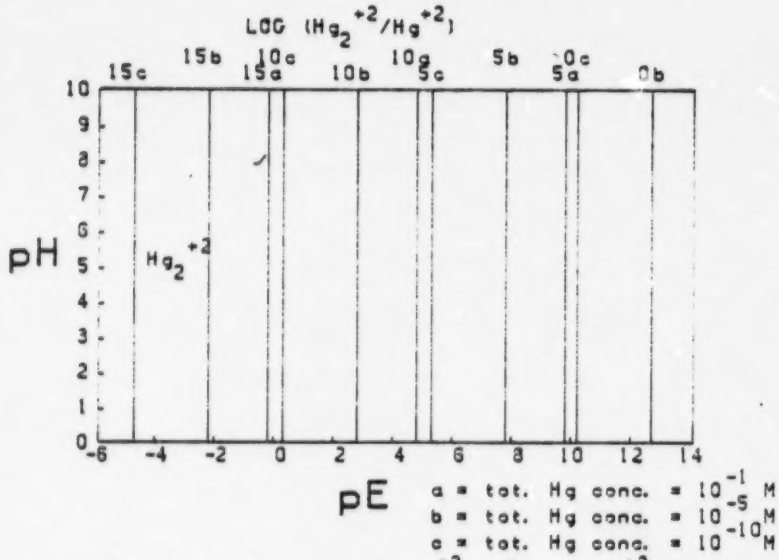


Figure D4. pH-pE. Reaction 4 $2Hg^{+2}+2e^{-} \rightarrow Hg_2^{+2}$ (aq)

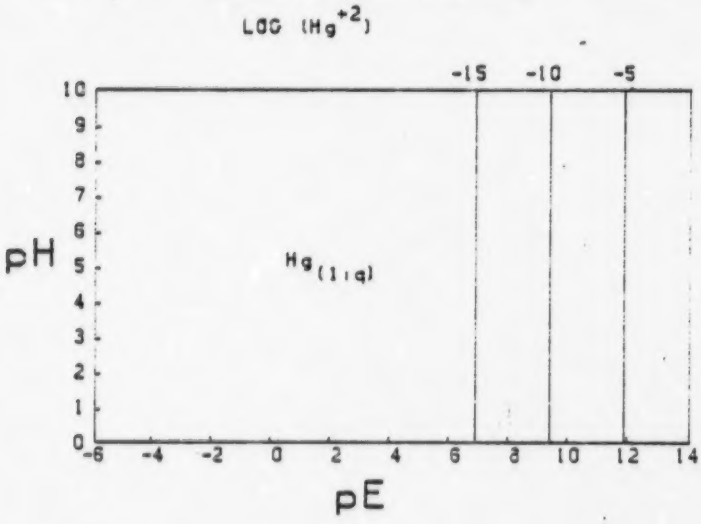


Figure D3. pH-pE. Reaction 3 $Hg^{+2}+2e^{-} \rightarrow Hg_{(liq)}$

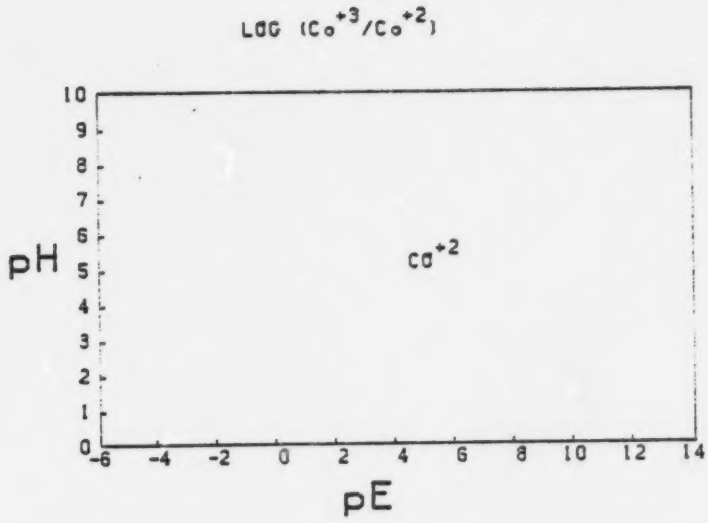


Figure 06. pH-pE. Reaction 6 $Co^{+2} \rightarrow Co^{+3} + e^-$

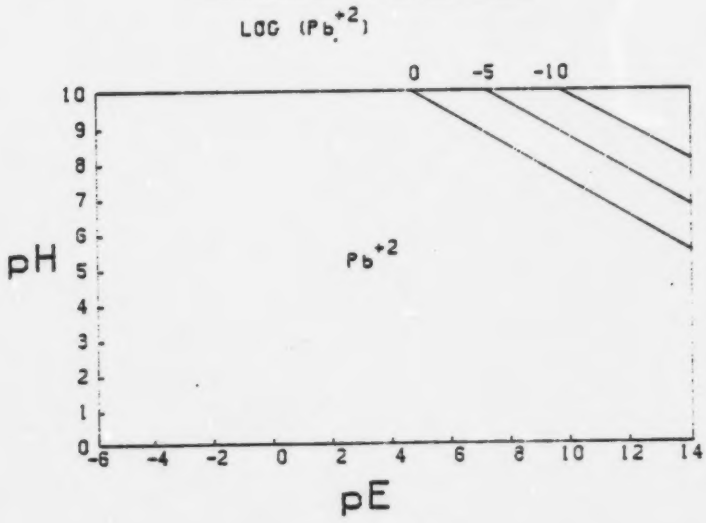


Figure 05. pH-pE. Reaction 5 $Pb^{+2} + 2H_2O \rightarrow PbO_{2(s)} + 4H^+ + 2e^-$

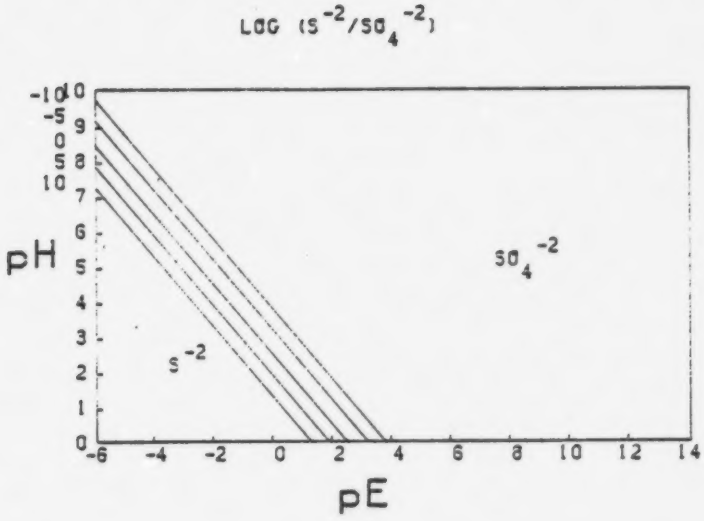


Figure D8. pH-pE. Reaction 8 $SO_4^{-2}+8H^++8e^- \rightarrow S^{-2}+4H_2O$

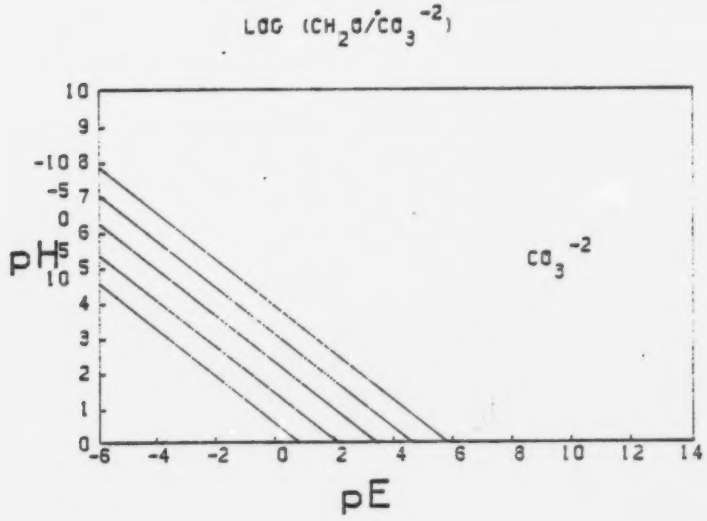


Figure D7. pH-pE. Reaction 7 $CO_3^{-2}+6H^++4e^- \rightarrow CH_2O_{(aq)}+2H_2O$

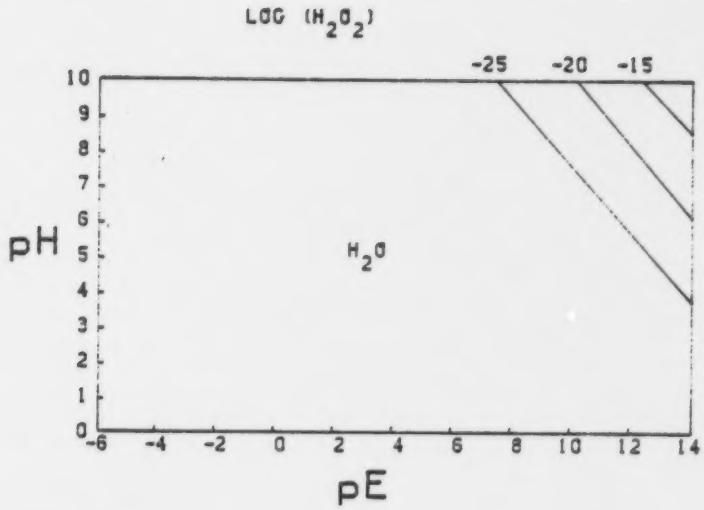


Figure D10. pH-pE. Reaction 10 $2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$

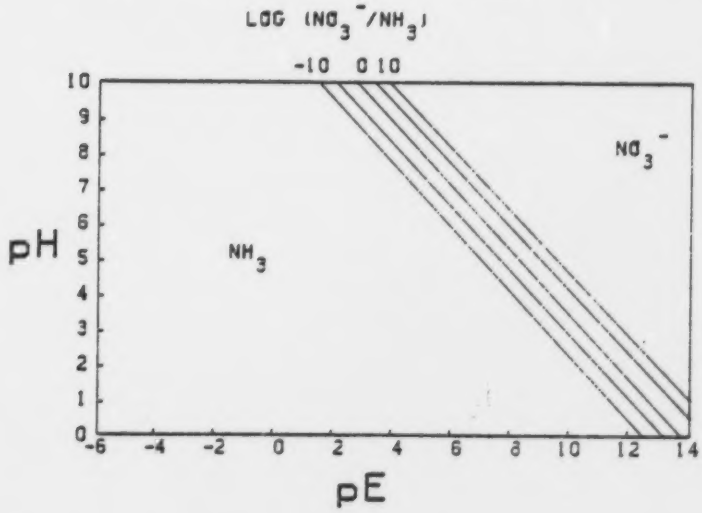


Figure D9. pH-pE. Reaction 9 $NH_{3(aq)} + 3H_2O \rightarrow NO_3^- + 9H^+ + 8e^-$

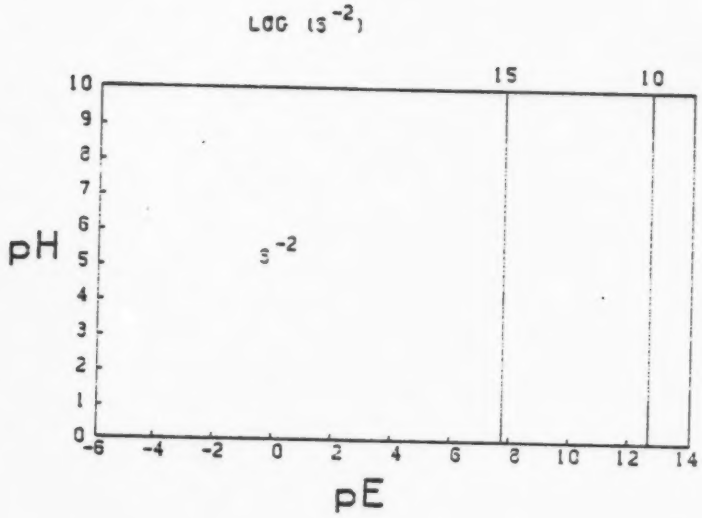


Figure D12. pH-pE. Reaction 12 $FeS_{2(s)} + 2e^- \longrightarrow Fe^{+2} + 2S^{-2}$

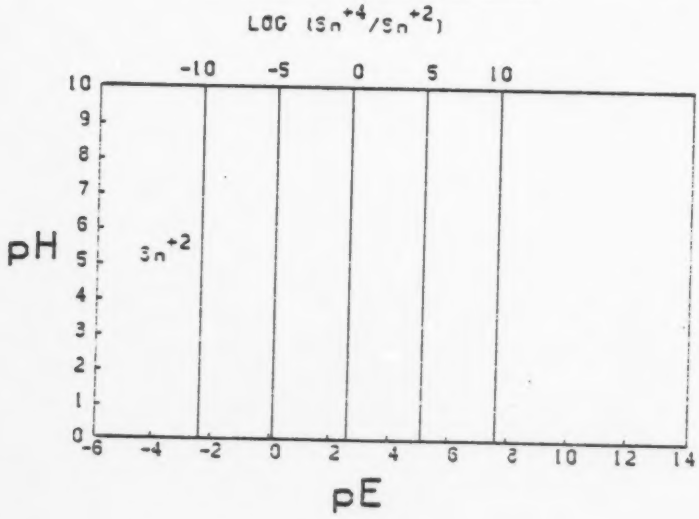


Figure D11. pH-pE. Reaction 11 $Sn^{+2} \longrightarrow Sn^{+4} + 2e^-$

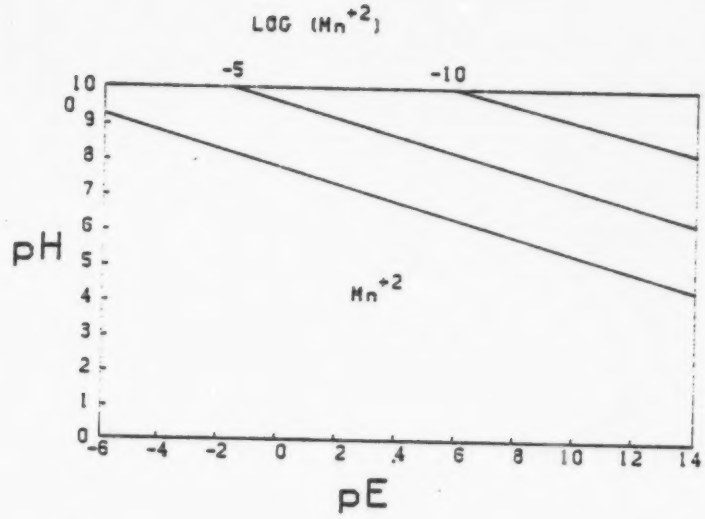


Figure D14. pH-pE. Reaction 14 $3Mn^{+2}+4H_2O \rightarrow Mn_3O_{4(s)}+8H^++2e^-$

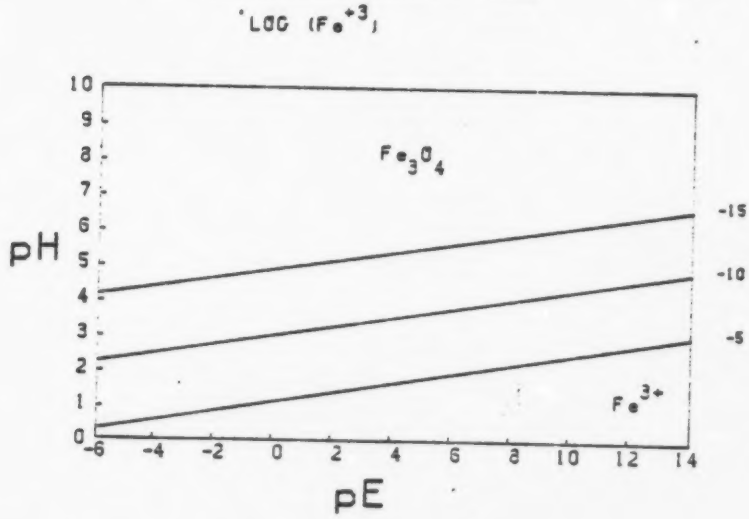


Figure D13. pH-pE. Reaction 13 $3Fe^{+3}+4H_2O+e^- \rightarrow Fe_3O_{4(s)}+8H^+$

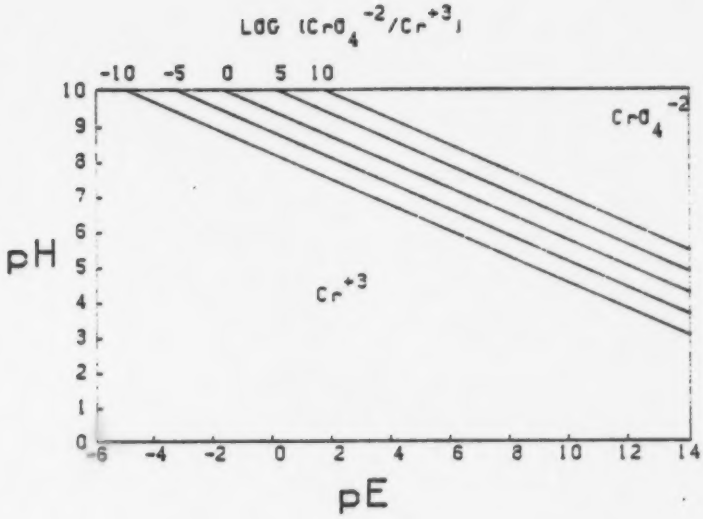


Figure D16. pH-pE. Reaction 16 $Cr^{+3}+4H_2O \rightarrow CrO_4^{-2}+8H^{+}+3e^{-}$

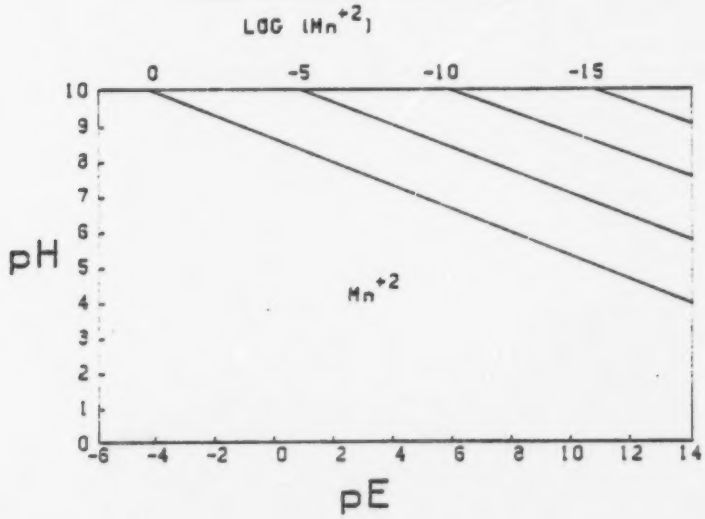


Figure D15. pH-pE. Reaction 15 $Mn^{+2}+2H_2O \rightarrow MnO(OH)_{(s)}+3H^{+}+e^{-}$

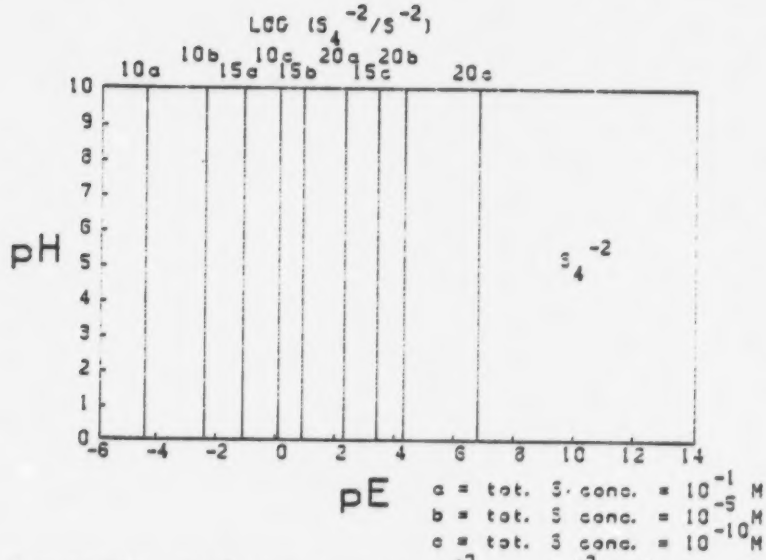


Figure D18. pH-pE. Reaction 18 $4S^{-2} \rightarrow S_4^{-2} + 6e^-$

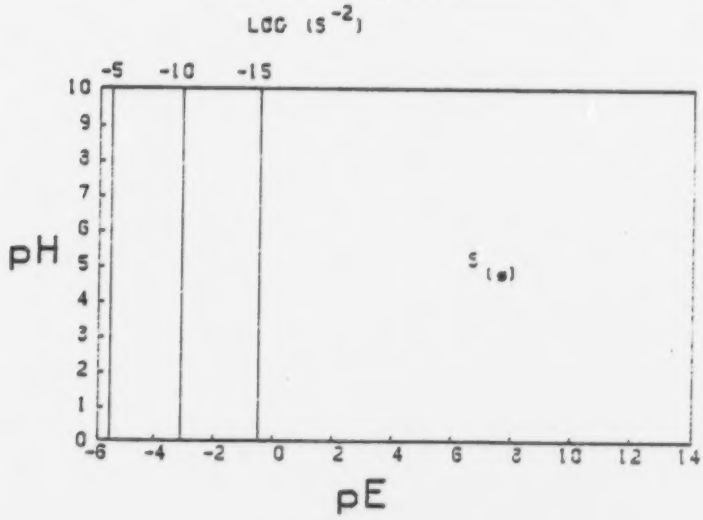


Figure D17. pH-pE. Reaction 17 $S^{-2} \rightarrow S_{(s)} + 2e^-$

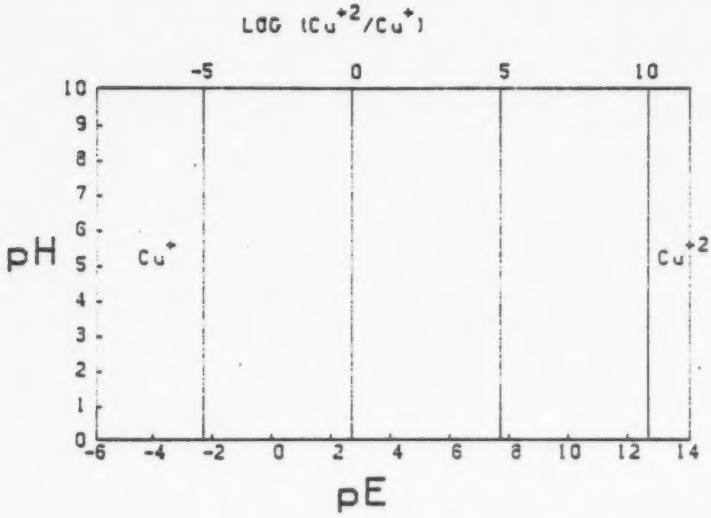


Figure D20. pH-pE. Reaction 20 $Cu^{+} \rightarrow Cu^{+2} + e^{-}$

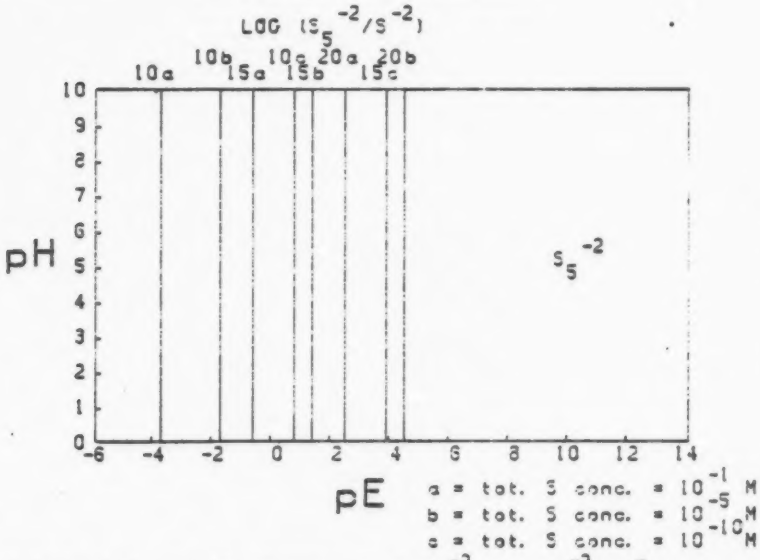


Figure D19. pH-pE. Reaction 19 $S^{-2} \rightarrow S_5^{-2} + 8e^{-}$

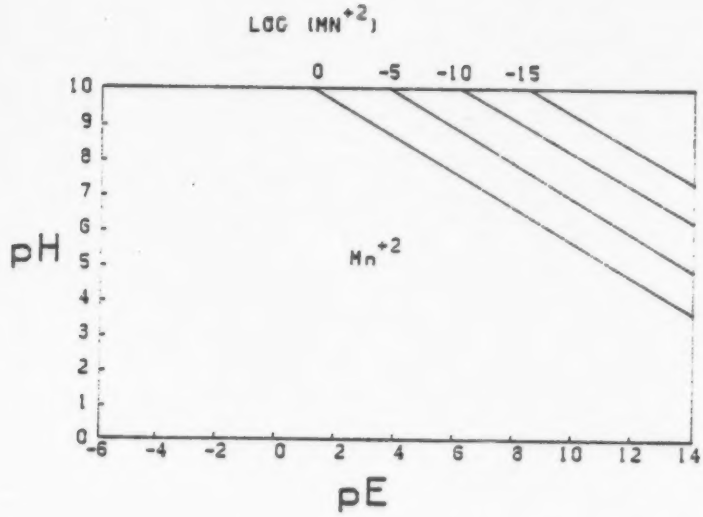


Figure D22. pH-pE. Reaction 22 $Mn^{+2}+2H_2O \rightarrow MnO_{2(s)}+4H^{+}+2e^{-}$

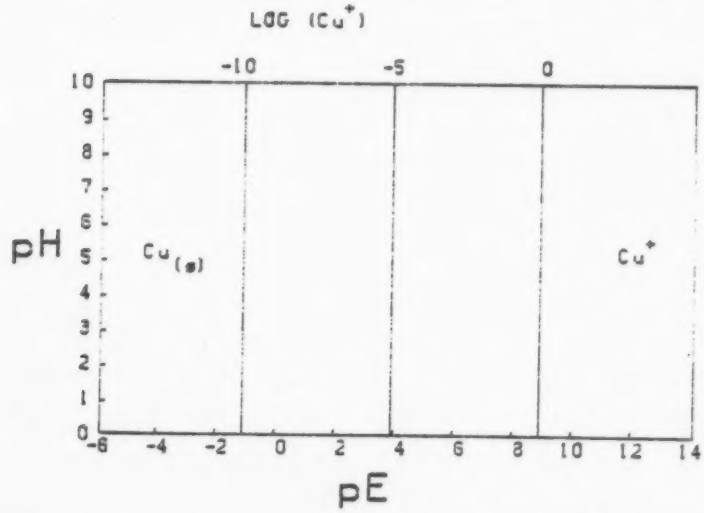


Figure D21. pH-pE. Reaction 21 $Cu^{+}+e^{-} \rightarrow Cu_{(s)}$

APPENDIX E: MIXED SOLIDS

Ref. No.	log K	Name in Printout	Name	Formula from Data Base
1	-4.9	CHLORITE	Chlorite	$Mg_5Al_2(SiO_2(OH)_2)_3 - 10H^+$
2	1387.4	ILLITE	Illite	$K_{12}Mg_5Al_{46}(SiO_2(OH)_2)_{70} - 20H^+$
3	67.1	MICCLINE	Microcline	$KAl(SiO_2(OH)_2)_3 + 2H^+$
4	232.3	NA-MONT	Na-Montmorillonite	$NaAl_7(SiO_2(OH)_2)_{11}$
5	17.0	DOLOMITE	Dolomite	$CaMg(CO_3)_2$
6	80.4	PBPO4CL	$Pb_5(PO_4)_3Cl$	$Pb_5(PO_4)_3Cl$
7	67.4	ADULARIA	Adularia	$KAl(SiO_2(OH)_2)_3 + 2H^+$
8	64.8	ALBITE	Albite	$NaAl(SiO_2(OH)_2)_3 + 2H^+$
9	21.3	ANORTHIT	Anorthite	$CaAl_2(SiO_2(OH)_2)_2 - 4H^+$
10	36.6	ANALCIME	Analcime	$NaAl(SiO_2(OH)_2)_2$
11	51.8	K-MICA	Muscovite	$KAl_3(SiO_2(OH)_2)_3 - 4H^+$
12	1.3	ALUNITE	Alunite	$KAl_3(SO_4)_2 - 6H^+$
13	133.4	PHLLPSIT	Phillipsite	$KNaAl_2(SiO_2(OH)_2))_6 + 4H^+$
14	62.3	F-APATIT	Fluor-apatite	$Ca_5F(PO_4)3$
15	45.6	ANNITE	Annite	$KFeAl(SiO_2(OH)_2)_3 - 4H^+$
16	30.0	HUNTITE	Huntite	$CaMg_3(CO_3)_4$
17	78.6	LAUMNTIT	Laumontite	$CaAl_2(SiO_2(OH)_2)_4$
18	36.4	PREHNITE	Prehnite	$Ca_2Al_2(Si_2(OH)_2)_3 - 4H^+$
19	165.2	LEONHARD	Leonhardite	$Ca_2Al_4(SiO_2(OH)_2)_8$
20	74.4	WAIRAKIT	Wairakite	$CaAl_2(SiO_2(OH)_2)_4$

21	234.2	K-MONT	K-Montmorillonite	$KAl_7(SiO_2(OH)_2)_{11}$
22	468.0	CA-MONT	Ca-Montmorillonite	$CaAl_{14}(SiO_2(OH)_2)_{22}$
23	468.5	MG-MONT	Mg-Montmorillonite	$MgAl_{14}(SiO_2(OH)_2)_{22}$
24	63.0	CD2FECN6	Cd-ferrocyanide	$Cd_2Fe(CN)_6$
25	61.3	ZN2FECN6	Zn-ferrocyanide	$Zn_2Fe(CN)_6$
26	63.6	PB2FECN6	Pb-ferrocyanide	$Pb_2Fe(CN)_6$
27	89.7	AG4FECN6	Ag-ferrocyanide	$Ag_4Fe(CN)_6$

APPENDIX F: Use of the Interactive Version, EQLINTR

EQLINTR is a modified version of REDEQL-UMD that allows the user to interactively input data for a speciation calculation. Use of this version of the program is especially advantageous in any or all of the following situations: 1) if the user has immediate access to a computer terminal and wishes to have a quick, local return of speciation results, 2) if the user wishes to temporarily add complexes and/or solids and associated thermodynamic data to the data base at run time without modifying the permanent data base, 3) if the user wishes to edit equilibrium constants and or stoichiometries for complexes and/or solids, 4) if the user has only a 80-column output computer terminal, 5) if the user prefers a free field format as compared to a fixed field format as required by the batch version, 6) if the user wishes to assign the task of data entry to a laboratory technician, and 7) if the user wishes to exert fine control over the type and amount of output.

In order to accomplish the above, the following changes were made in REDEQL-UMD: 1) input routines were modified to allow input in a time- sharing mode, and 2) overlays were used in order to cut down the over-all field length to less than the maximum allowed for time-share use. EQLINTR still retains the full capabilities described previously in this manual.

To use this version, EQLINTR is compiled using MNF, a FORTRAN compiler. After making a copy of the thermodynamic data file available in the local mode as TAPE10, the binary compilation of EQLINTR is excuted by simply issuing the command "bfname.", where bfname is the name of the binary file created at compile time. The program begins by printing out, on the terminal, the version of EQLINTR being used and the associated data base date. The program then issues a series of prompts, each followed by a question mark. After each question mark the program expects that you will enter a response followed by a carriage return. The very first prompt asks whether you wish to run in an interactive mode, which is usually the case, or whether you wish to have the program read data from a disc file, TAPE15. TAPE15 would be set up as an exact duplicate of a card deck structure as described in the users guide. The purpose of this option is facilitate running a batch job from the terminal. If the user wishes to input data in an interactive format, succeeding prompts will be for number of metals, ligands, cases, pH, etc. These questions may be answered with the word "help" in which case a short explanation of the expected input is given. Of course, the material from the USERS MANUAL is also of value.

APPENDIX G: Users Manual for TEMCORR

TEMCORR, an auxiliary program for management of data for the program REDEQL-UMD, serves two functions:

1) Upon user specification of the components in the system under study, TEMCORR edits the Thermodynamic Data File, retaining only those data relevant to this study. The resulting smaller data base can save considerable computer time in later calculations.

2) The data for the specified components may be adjusted to provide a value appropriate to a temperature other than 25°C. To do this, TEMCORR merges data from the UMDEQ Thermodynamic Data File with data from an enthalpy data file. When the enthalpy data file does not contain a value corresponding to an entry in the Themodynamic Data File, the user may choose either to eliminate the entry in the Thermodynamic Data File or to use the entry without adjustment to the new temperature. For temperatures other than 25°C the program can list, as output, missing enthalpy values (short list) or, for the components specified, list all entries in the Thermodynamic Data File before and after adjustment for temperature (long list). Those that could not be corrected because corresponding enthalpy values were not found are flagged in the long list. TEMCORR will of course work with any data and enthalpy files which have the proper format. A description of the associated enthalpy data file (THERMO) is included.

The temperature adjustments, when made, are effected using the equation:

$$\ln K_2 = \ln K_{298} + H^o(T_2-298)/(298RT_2)$$

where K_2 is the final stability constant for the new temperature,
T_2 is final temperatures in °K,
and R is the universal gas constant.

The program requires up to five types of input cards. These are described in Table 1. Card Types (1), (3), (4), and (5) are always used, while Card Type (2) is used only when T_2 does not equal 25°C.

The format of the data file from which the stability constants are read and in which the selected and corrected constants are written is described in the REDEQL-UMD USERS GUIDE. The data in this file must be read and will be printed without decimal points by TEMCORR.

The formats for the enthalpy data file are shown in Table 2. Card Type

Table 1. Input Cards for TEMCORR

Card Type	Field(s)	Card Column(s)	Description
(1)			Temperature card(^{o}C) Format F6.2 1 card required
	1	1-6	Temperature for which data file will be created.
(2)			Enthalpy Options Card. Format I1,1X,I1. 1 card, required if T not equal to 25°C
	1	1	If no enthalpy value, 1 = use 25°C constant 2 = don't use any constant
	2	3	For corrected data, 0 = print no list 1 = list which enthalpy values are missing 2 = list old and new formation constants
(3)			Numbers of Metals and Ligands Format I3,1X,I3 1 card required
	1	2-3	Number of metals (excluding H^{+})
	2	5-6	Number of ligands (excluding OH^{-})
(4)			List of Metal Reference Numbers Format 26(I2,1X) Requires as many cards as necessary to list the number of metals shown on Card (3), field 1.
	1	1-2	Reference number of first metal
	2	4-5	Reference number of second metal
	3	7-8	etc.
(5)			List of Ligand Reference Numbers Format 26(I2,1X) Requires as many cards as necessary to list the number of ligands shown on Card 3, field 2.
	1	1-2	Reference number of first ligand.
	2	4-5	Reference number of second ligand.
	3	7-8	etc.

Table 2. Format of Enthalpy Data File

Card Type	Field(s)	Card Column(s)	Description
(0)			Deck Identification Card Format 3A2. 1 card required.
	1	1-2	Month of the enthalpy data file
	2	3-4	Day of the data file
	3	5-6	Year of the data file
(1)			Header for Solid, Complexes, and Special Enthalpy Values Format I3,3X,3I6. 1 card required.
	1	1-3	Number of pairs for which enthalpy data are given.
	2	7-12	100 x H^o for the ionization of water.
	3	13-18	100 x H^o for the reaction $2H^+ + CO_3^{2-} \longrightarrow CO_2(g) + H_2O$
	4	19-24	100 x H^o for the reaction $2H_2O \longrightarrow O_2(aq) + 4H^+ + 4e-$
(2)			Solid or Complex Enthalpy Cards Format A1,2I3,6I6 Number of cards = 2 x number of pairs shown in Card (1), field 1. If there are two pairs of cards for formation constants there should be two pairs of enthalpy cards. Pairs must be in ascending numerical order (metals first then ligands).
	1	1	S or C for solid or complex
	2	3-4	Metal reference number
	3	6-7	Ligand reference number
	4	8-13	100 x H^o for first solid or complex listed in thermodynamic data file.

Table 2 (continued)

Card Type	Field(s)	Card Column(s)	Description
	5	14-19	100 x H^o for the second solid or complex listed.
	6	20-25	100 x H^o for the third solid/complex.
	7	26-31	100 x H^o for the fourth/complex.
	8	32-37	100 x H^o for the fifth solid/complex.
	9	38-43	100 x H^o for the sixth solid/complex.
(3)			Redox Header Card Format I3. 1 card required.
	1	1-3	Number of redox reactions for which H^o is given.
(4)			Redox Enthalpy Cards. Format I3,I6 Number of cards required equals number on Card (3), field 1.
	1	1-3	Number of the redox reaction
	2	4-10	100 x H^o for the reaction
(5)			Mixed Solid Header Card Format I3 1 card required
	1	1-3	Number of mixed solids for which H^o is given.
(6)			Mixed Solids Enthalpy Cards Format I3,I6. Number of cards required equals number given on header Card (5), field 1.
	1	1-3	Mixed solid number
	2	4-10	100 x H^o.
(7)			Mixed Complex Header Card Format 2I3
	1	1-3	Number of triplets for which enthalpy values are

Table 2 (continued)

Card Type	Field(s)	Card Column(s)	Description
			given.
	2	4-6	Number of metal-metal-ligand triplets.
(8)			Mixed Complex Enthalpy Cards Format 3I3,A1,5I6 Number of cards required equals number shown on header cards. Cards must be in ascending numerical order when the triplet numbers are viewed as a single integer. All complexes which have a metal as the third ion must follow complexes with ligands as the third ion. The same triplet may be given on successive cards if that triplet has more than five stability constants.
	1	1-3	Reference number of the metal
	2	4-6	Reference number of the ligand
	3	7-9	Reference number of the third ion
	4	10	M or L for metal or ligand as third ion.
	5	11-16	100 x H^o for the first complex.
	6	17-22	100 x H^o for the second complex.
	7	23-28	100 x H^o for the third complex.
	8	29-34	100 x H^o for the fourth complex.
	9	35-40	100 x H^o for the fifth complex.

numbers are not contained in the actual data file but are used in this manual for easy reference. This file also must have no decimal points. Within each group (complexes/solids, redox reactions, etc.) the metal and ligand reference numbers for the enthalpy cards must be in ascending numerical order. When two or three reference numbers identify a card, they are treated as one large number with the blanks read as zero. The only exception to this ordering is within mixed complexes where all mixed complexes containing two ligands are entered prior to entering mixed complexes containing two metals. The ordering within each of the sets of mixed complexes is as described above.

Uses of this program are illustrated with a sample case of four metals and four ligands with the data adjusted for a temperature of 20.0°C. Card Type numbers are not included on input data cards but are used in this discussion for reference purposes. Two input decks are shown. The first (Figure 1) is for a "short list" (list of complexes, solids, etc. for which enthalpy values are missing), and causes to be excluded from the final data base all constants for which there were no corresponding enthalpy values in the data base THERMO.

```
  20.0
2 1
  4   4
 1  2  5 11
 1  5  6  3
```

Figure 1. Input cards for first example.

Briefly reviewing the five input cards in Figure 1.

(1) The temperature is 20°C.
(2) 2 = exclude constants if no corresponding enthalpy value
    1 = short list
(3) 4 metals and 4 ligands
(4) The metals are 1, 2, 5, 11 (Ca^{2+}, Mg^{2+}, Na^{+}, Cd^{2+})
(5) The ligands are 1, 5, 6, 3 (CO_3^{2-}, Br^{-}, I^{-}, Cl^{-})

The outputs which are produced are the "short list" (Figure 2) showing which items were omitted, e.g. the first solid of metal 1, ligand 99 had no enthalpy data, and the new Thermodynamic Data File at 20°C (Figure 3). This latter file is in the proper format for REDEQL-UMD.

The second deck, shown in Figure 4, is identical except that a "long list"

(both 25°C and 20°C formation constants) is requested and constants from 25°C are used if enthalpy values are not available. Figure 5 shows the "long list" and Figure 6 shows the new stability constants. (The first 12 lines of

```
TEMCORR--TEMPERATURE CORRECTION OF "UMDEQ" DATA BASE
     USING "UMDEQ" DATA OF    08-01-80
     AND THERMO DATA OF      08-01-80


SOLIDS AND COMPLEXES
    1099 S1
    2001          S3
    2003                          C1
    2005                          C1
    2099                              C2
    5001                          C1
    5099                          C1
   11001 S1                       C1  C2
   11003                                         C5
   11099     S2                       C2  C3  C4


REDOXES


MIXED SOLIDS


MIXED LIGAND COMPLEXES
11003005 MC1 MC2 MC3 MC4 MC5
11003006 MC1 MC2 MC3 MC4 MC5
11005006 MC1 MC2 MC3 MC4 MC5
MIXED METAL COMPLEXES
```

Figure 2. "Short list" of missing enthalpy values for first example.

```
23160      20.00
 5  5 -11.38      .288
 1  2     .99    40.080  CA +2
 2  2     .66    24.320  MG +2
 5  1     .97    22.991  NA +1
11  2     .97   112.410  CD +2
50  1    1.54     1.008  H  +1
 1 -2    1.00    60.011  CO3 -2
 3 -1    1.00    35.457  CL -1
 5 -1    1.00    79.916  BR -1
 6 -1    1.00   126.910  I  -1
99 -1    1.00    17.008  OH -1
  12 1383 1813-.0046
  1  1  840 1 1  0  834 1 1  0     0            0            0            0
        318 1 1  0 1136 1 1  1     0            0            0            0
  1 99    0            0            0            0            0            0
     -1265 1 0 -1     0            0            0            0            0
  2  1  753 1 1  0  472 1 1  0     0         -968 2 1 -2  942 5 4 -2     0
        288 1 1  0 1136 1 1  1     0            0            0            0
  2 99-1651 1 0 -2     0            0            0            0            0
     -1124 1 0 -1     0            0            0            0            0
  5  1  111 2 1  0   -9 2 1  0 1078 1 1  1 1130 3 2  1     0            0
         0            0            0            0            0            0
  5  3 -159 1 1  0     0            0            0            0            0
     -186 1 1  0     0            0            0            0            0
  5  5    0            0            0            0            0            0
     -313 1 1  0     0            0            0            0            0
 11  3    0            0            0            0            0            0
        198 1 1  0  261 1 2  0  243 1 3  0  177 1 4  0     0            0
 11  5    0            0            0            0            0            0
        212 1 1  0  298 1 2  012801 1 3  0  290 1 4  0     0            0
 11  6    0            0            0            0            0            0
        225 1 1  0  388 1 2  0  494 1 3  0  589 1 4  0     0            0
 11 99-1335 1 0 -2     0            0            0            0            0
     -991 1 0 -1     0            0            0        -925 2 0 -1-3232 4 0 -4
 50  1    0            0            0            0            0            0
     1028 0 1  1 1661 0 1. 2     0            0            0            0
  2
  7   50    1    3   -4    6  1306    0    1CH20
 10   50   99    1    2   -2 -5846    0    0H2O2
  2
  5    0    1    2    1   99    1    1    2    0    0  1710    0   0DOLOMITE
 16    0    1    2    1   99    1    3    4    0    0  3032    0   0HUNTITE
 0
```

Figure 3. New Thermodynamic Data File for first example.

Figure 6 would have been identical to Figure 3 and are not repeated.) Note that the Thermodynamic Data File for the second example is larger than that for the first because constants were retained whether or not an enthalpy value existed to allow for adjustment to the new temperature.

```
  20.0
1 2
  4   4
 1  2  5 11
 1  5  6  3
```

Figure 4. Input cards for second example.

```
TEMCORR--TEMPERATURE CORRECTION OF "UNDEG" DATA BASE
    USING "VIDEO" DATA OF    88-01-10
    AND THERMO DATA OF       88-01-08

SOLIDS AND COMPLEXES
                 S1      S2      S3      S4      S5      S6      C1      C2      C3      C4      C5      C6
  1001 OLD      637     631       0       0       0       0     315    1133       0       0       0       0
       NEW      640     634       0       0       0       0     318    1136       0       0       0       0
  1099 OLD    -2281       0       0       0       0       0   -1265       0       0       0       0       0
       NEW ** -2281       0       0       0       0       0   -1265       0       0       0       0       0
  2001 OLD      746     467     454   -1081     877       0     288    1120       0       0       0       0
       NEW      753     472 **  454    -960     942       0     288    1136       0       0       0       0
  2003 OLD        0       0       0       0       0       0    -100       0       0       0       0       0
       NEW        0       0       0       0       0       0 **  -100       0       0       0       0       0
  2005 OLD        0       0       0       0       0       0    -140       0       0       0       0       0
       NEW        0       0       0       0       0       0 **  -140       0       0       0       0       0
  2099 OLD    -1664       0       0       0       0       0   -1144   -3971       0       0       0       0
       NEW    -1651       0       0       0       0       0   -1124 ** -3971       0       0       0       0
  5001 OLD      131     -13    1086    1112       0       0     120       0       0       0       0       0
       NEW      111      -9    1074    1130       0       0 **  120       0       0       0       0       0
  5003 OLD     -158       0       0       0       0       0    -105       0       0       0       0       0
       NEW     -159       0       0       0       0       0    -106       0       0       0       0       0
  5005 OLD        0       0       0       0       0       0    -310       0       0       0       0       0
       NEW        0       0       0       0       0       0    -313       0       0       0       0       0
  5999 OLD        0       0       0       0       0       0   -1410       0       0       0       0       0
       NEW        0       0       0       0       0       0 **-1410       0       0       0       0       0
 11001 OLD     1374       0       0       0       0       0     540    1220       0       0       0       0
       NEW **  1374       0       0       0       0       0 **  540 **  1220       0       0       0       0
 11003 OLD        0       0       0       0       0       0     196     260     248     178    -678       0
       NEW        0       0       0       0       0       0     196     261     243     177 **  -678       0
 11005 OLD        0       0       0       0       0       0     214     308     308     290       0       0
       NEW        0       0       0       0       0       0     212     296   12001     290       0       0
 11006 OLD        0       0       0       0       0       0     228     392     588     688       0       0
       NEW        0       0       0       0       0       0     225     386     494     589       0       0
 11099 OLD    -1364   -1363       0       0       0       0   -1006   -2035   -3330   -4735    -939   -3205
       NEW    -1330 ** -1363       0       0       0       0    -991 ** -2035 ** -3330 ** -4735    -925   -3232
 50001 OLD        0       0       0       0       0       0    1033    1460       0       0       0       0
       NEW        0       0       0       0       0       0    1026    1461       0       0       0       0

REDOXES
NUMBER    OLD    NEW
  7      1328   1306
 10     -5968  -5046

MIXED SOLIDS
NUMBER    OLD    NEW
  5      1700   1710
 16      3000   3022

MIXED LIGAND COMPLEXES
                 MC1     MC2     MC3     MC4     MC5
11003005 OLD     426     584     644     637     687
       NEW **    426 **  584 **  644 **  637 **  687
11003006 OLD     454     522     647       0       0
       NEW **    454 **  522 **  647 **    0 **    0
11005006 OLD     485     488     615     674     625
       NEW **    485 **  488 **  615 **  674 **  625
MIXED METAL COMPLEXES
```

Figure 5. "Long list" of 20 and 25 degree celcius formation constants for second example.

```
16 1383 1813-.0046
 1  1  840 1 1  0  834 1 1  0     0            0            0            0
       318 1 1  0 1136 1 1  1     0            0            0            0
 1 99-2281 1 0 -2     0            0            0            0            0
     -1265 1 0 -1     0            0            0            0            0
 2  1  753 1 1  0  472 1 1  0  454 1 1  0 -968 2 1 -2  942 5 4 -2         0
       288 1 1  0 1136 1 1  1     0            0            0            0
 2  3    0            0            0            0            0            0
     -100 1 1  0     0            0            0            0            0
 2  5    0            0            0            0            0            0
     -140 1 1  0     0            0            0            0            0
 2 99-1651 1 0 -2     0            0            0            0            0
    -1124 1 0 -1-3971 4 0 -4      0            0            0            0
 5  1  111 2 1  0    -9 2 1  0 1078 1 1  1 1130 3 2  1      0            0
       120 1 1  0     0            0            0            0            0
 5  3 -159 1 1  0     0            0            0            0            0
     -186 1 1  0     0            0            0            0            0
 5  5    0            0            0            0            0            0
     -313 1 1  0     0            0            0            0            0
 5 99    0            0            0            0            0            0
    -1418 1 0 -1     0            0            0            0            0
11  1 1374 1 1  0     0            0            0            0            0
       540 1 1  0 1220 1 1  1     0            0            0            0
11  3    0            0            0            0            0            0
       198 1 1  0  261 1 2  0  243 1 3  0  177 1 4  0 -670 1 1 -1         0
11  5    0            0            0            0            0            0
       212 1 1  0  298 1 2  012801 1 3  0  290 1 4  0      0            0
11  6    0            0            0            0            0            0
       225 1 1  0  388 1 2  0  494 1 3  0  589 1 4  0      0            0
11 99-1335 1 0 -2-1383 1 0 -2     0            0            0            0
     -991 1 0 -1-2035 1 0 -2-3330 1 0 -3-4735 1 0 -4 -925 2 0 -1-3232 4 0 -4
50  1    0            0            0            0            0            0
    1028 0 1  1 1661 0 1  2     0            0            0            0
  2
  7   50    1    3   -4    6  1306    0    1CH2O
 10   50   99    1    2   -2 -5846    0    0H2O2
  2
  5    0    1    2    1   99    1    1    2    0    0  1710    0    0DOLOMITE
 16    0    1    2    1   99    1    3    4    0    0  3032    0    0HUNTITE
  3
 11   3   5L  426 1 1 1  0  504 1 1 2  0  644 1 1 3  0  637 1 2 1  0  687 1 2 2  0
 11   3   6L  454 1 1 1  0  522 1 1 2  0  647 1 2 1  0    0 0 0 0 -0    0 0 0 0 -0
 11   5   6L  405 1 1 1  0  408 1 1 2  0  815 1 1 3  0  674 1 2 1  0  625 1 2 2  0
  0
```

Figure 6. Stability constants for the second example.